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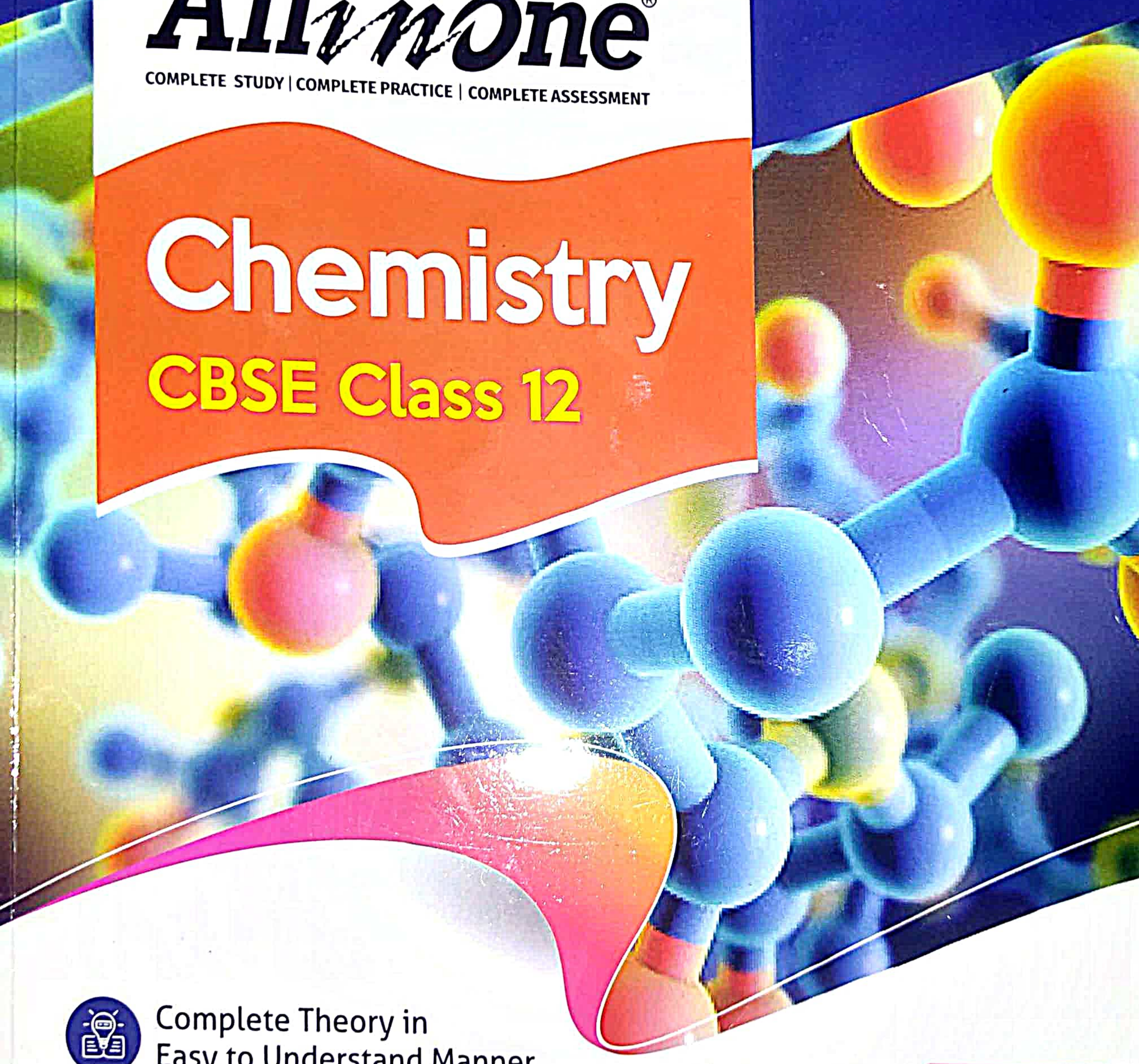
Chemistry

CBSE Class 12



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Chemistry

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ARIHANT PRAKASHAN (School Division Series)

CONTENTS

01

SOLUTIONS

In our daily life, we usually come across the substances which are mixtures of two or more pure substances. Solution is one of the most important classes of mixtures which is homogeneous in composition and properties.

The utility or importance of solutions in our life depends on their compositions. For instance 1 part per million (ppm) of fluoride ions in water prevents tooth decay, while 1.5 ppm causes the tooth to become mottled and high concentration of fluoride ions can be poisonous. e.g. Sodium fluoride in higher concentration is used in rat poisoning.

So, in this chapter, we will not only discuss the different types of solution and associated laws but also the concentration and related terms.

CHAPTER CHECKLIST

- Solutions, Terms Expressing Concentration of Solutions
- Solubility
- Vapour Pressure of Liquid Solutions
- Colligative Properties and Determination of Molar Mass

|TOPIC 1|

Solutions, Terms Expressing Concentration of Solutions

A solution is a homogeneous mixture of two or more substances whose composition can be varied within certain limits. Here, homogeneous mixture means that its composition and properties are uniform throughout the mixture. In such a mixture, the component that is present in the largest quantity is known as **solvent**. The one or more components present in the solution other than the solvent are called **solute**. The physical state in which solution exists is determined by the state of solvent.

Characteristics of Solutions

These are as follows:

(i) A solution is a single phase system.

(ii) A solution does not allow a beam of light to scatter.

(iii) The particles of solute in solution cannot be seen with naked eye.

(iv) A solution is stable and the solute from the solution cannot be separated by filtration process.

(v) The solute particles in a solution do not settle down.

CLASSIFICATION OF SOLUTIONS

Solutions are classified on different basis as follows :

On the Basis of Solvent

On the basis of solvent, the solution may be of the following types:

(i) **Aqueous solution** When solute is dissolved in water, it is known as aqueous solution. e.g. Ethanol in water.

(ii) **Non-aqueous solution** When solute is dissolved in a solvent other than water, it is known as non-aqueous solution, e.g. Iodine in alcohol (tincture of iodine).

On the Basis of Number of Components

On the basis of number of components, the solution may be of the following types:

(i) **Binary solution** The solution which contains two components is called binary solution, e.g. salt solution.

(ii) **Ternary solution** The solution which contains three components either two solvents and one solute or one solvent and two solutes is called ternary solutions. e.g. Salt, sugar and water solution.

The naming (binary, ternary, quaternary) goes on as the number of components increases. In this chapter, we will focus on binary solutions only.

On the Basis of Physical State of Components

On the basis of physical state of components, solution can be broadly divided into three types. Their further subdivisions and examples are tabulated below.

Types of solutions	Solute	Solvent	Examples
Solid solutions	Gas	Solid	Hydrogen in palladium.
	Liquid	Solid	Mercury with sodium forming an amalgam.
	Solid	Solid	Alloys like bronze and many others.
Liquid solutions	Gas	Liquid	Oxygen in water, aerated drinks, carbon dioxide in water.
	Liquid	Liquid	Alcoholic beverages are basically solutions of ethanol in water.
	Solid	Liquid	Sucrose (table sugar) or salt in water.
Gaseous solutions	Gas	Gas	Air which is mostly mixture of nitrogen and oxygen gases.
	Liquid	Gas	Chloroform mixed with nitrogen gas, humidity in air.
	Solid	Gas	Camphor in nitrogen gas, dust or smoke.

EXPRESSING CONCENTRATION OF SOLUTIONS

Composition of a solution can be described by expressing its concentration. The latter can be expressed either qualitatively or quantitatively, e.g. qualitatively we can say that the solution is dilute (i.e. relatively very small quantity of solute) or it is concentrated (i.e. relatively very large quantity of solute). The concentration of a solution may be defined as the amount of solute present in the given quantity of the solution. There are several methods by which we can describe the concentration of the solution:

Mass Percentage (w/w)

The mass percentage of a component in a given solution is the mass of the component per 100 g of the solution.

$$\text{Mass \% of a component} = \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100$$

Let, w_B be the mass of solute (B) and w_A be the mass of solvent (A), then

$$\boxed{\text{Mass percentage} = \frac{w_B}{w_A + w_B} \times 100}$$

e.g. A 10% glucose solution in water means that 10 g of glucose is dissolved in 90 g of water resulting in a 100 g of solution.

Concentration described by mass percentage is commonly used in industrial chemical applications, e.g. commercial bleaching solution contains 3.62 mass percentage of sodium hypochlorite in water.

EXAMPLE |1| Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4), if 22 g of benzene is dissolved in 122 g of CCl_4.

NCERT Intext

Sol. Mass of solution = Mass of benzene + Mass of carbon tetrachloride = $(22+122)\text{g} = 144\text{ g}$

$$\text{Mass \% of benzene} = \frac{\text{Mass of benzene}}{\text{Mass of solution}} \times 100 = \frac{22}{144} \times 100 = 15.28\%$$

$$\text{Mass \% of } CCl_4 = \frac{\text{Mass of } CCl_4}{\text{Mass of solution}} \times 100 = \frac{122}{144} \times 100 = 84.72\%$$

Volume Percentage (V/V)

The volume percentage is the volume of the component per 100 parts by volume of the solution.

$$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of solution}} \times 100$$

Solutions containing liquids are commonly expressed in volume percentage, e.g. 100 mL of 35% (*V/V*) solution of ethylene glycol contains 35 mL of ethylene glycol and 65 mL of water. This solution is used as an antifreeze in cars for proper working of the engine during cold winter.

At this concentration, the antifreeze lowers the freezing point of water to 255.4 K(–17.6°C).

EXAMPLE |2| What amount of water is required to make 10% ethanol in water solution using 10 mL of pure ethanol?

Sol. Given, volume of pure ethanol = 10 mL

volume% of ethanol = 10%

Total amount of solution = ?

$$\text{Volume\% of ethanol} = \frac{\text{Volume of ethanol}}{\text{Total volume of solution}} \times 100$$

or

$$10 = \frac{10}{\text{Total volume of solution}} \times 100$$

$\Rightarrow$ Total volume of solution = 100 mL

Thus, the amount of water used = 100 – amount of ethanol

$= 100 - 10 = 90\,\text{mL}$

Mass by Volume Percentage (*w*/*V*)

It is the mass of solute dissolved in 100 mL of the solution.

$$\text{Mass by volume \%} = \frac{\text{Mass of solute}}{\text{Total volume of solution}} \times 100$$

e.g. A 10% solution of sodium chloride (*w*/*V*) means that 10 g of sodium chloride is dissolved in 100 mL of solution. This unit is commonly used in medicines and pharmacy.

Parts Per Million (ppm)

When a solute is present in trace quantities, the concentration is expressed in parts per million (ppm).

$$\text{ppm} = \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

Concentration in parts per million can also be expressed as mass to mass, volume to volume and mass to volume. e.g.

(i) The concentration of pollutants in water or atmosphere is often expressed in terms of $\mu g\, mL^{-1}$ or ppm.

(ii) Gases dissolved in water is expressed in $mg\, kg^{-1}$ or ppm.

EXAMPLE |3| If 1 L of a solution contains 5 mL of a certain disinfectant then express this concentration in ppm.

Sol. Amount of disinfectant = 5 mL = 5×10^{-3} L

Amount of solution = 1 L

Then, $$\text{ppm} = \frac{\text{Amount of disinfectant}}{\text{Amount of solution}} \times 10^6$$

$$= \frac{5 \times 10^{-3}}{1} \times 10^6 = 5 \times 10^3 \text{ ppm}$$

Mole Fraction (χ)

It is the ratio of number of moles of one component to the total number of moles of all the components present in the solution. Commonly used symbol for mole fraction is χ.

Mole fraction of a component

$$= \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

Mole fraction of solute

$$\chi_{(\text{solute})} = \frac{n_{(\text{solute})}}{n_{(\text{solute})} + n_{(\text{solvent})}}$$

Mole fraction of solvent

$$\chi_{(\text{solvent})} = \frac{n_{(\text{solvent})}}{n_{(\text{solute})} + n_{(\text{solvent})}}$$

where, n_{solute} and n_{solvent} are the number of moles of solute and solvent respectively.

e.g. In a binary solution, if the number of moles of *A* and *B* are n_A and n_B respectively, then mole fraction of *A* will be $$\chi_A = \frac{n_A}{n_A + n_B}$$

Similarly, mole fraction of *B*,

$$\chi_B = \frac{n_B}{n_A + n_B}$$

$$\therefore \quad \chi_A + \chi_B = 1$$

Mole fraction is independent of temperature and it is a dimensionless quantity. For a solution containing *i* number of components, we have

$$\chi_i = \frac{n_i}{n_1 + n_2 + \dots + n_i} = \frac{n_i}{\sum n_i}$$

It can be shown that for a given solution, sum of all the mole fractions is unity, i.e.

$$\chi_1 + \chi_2 + \dots + \chi_i = 1$$

Mole fraction unit is very useful in relating some physical properties of solutions, e.g, Vapour pressure with the concentration of the solution. It is also useful in describing the calculations involving gas mixtures.

EXAMPLE |4| Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

NCERT Intext

Sol. For 100 g of solution, mass of benzene in the solution = 30 g

[As, benzene in CCl_4 = 30%]

$\therefore$ Mass of carbon tetrachloride = (100 − 30) g = 70 g

Molar mass of benzene $(C_6H_6) = 12\times 6 + 1\times 6 = 78\text{ g mol}^{-1}$

Molar mass of $CCl_4 = 12 + 4\times 35.5 = 154\text{ g mol}^{-1}$

$$\therefore \text{Number of moles of benzene} = \frac{\text{Mass of benzene}}{\text{Molar mass of benzene}}$$

$$\text{Number of moles of benzene} = \frac{30\text{ g}}{78\text{ g mol}^{-1}} = 0.385\text{ mol}$$

$$\text{Number of moles of } CCl_4 = \frac{\text{Mass of } CCl_4}{\text{Molar mass of } CCl_4}$$

$$= \frac{70\text{ g}}{154\text{ g mol}^{-1}} = 0.455\text{ mol}$$

$$\text{Mole fraction of benzene } (\chi_1) = \frac{\text{Moles of benzene}}{\text{Total moles in the solution}}$$

$$= \frac{0.385}{0.385 + 0.455}$$

$$= \frac{0.385}{0.84} = 0.458$$

And mole fraction of CCl_4 $(\chi_2) = 1 - 0.458 = 0.542$

(as $\chi_1 + \chi_2 = 1$)

Molarity (*M*)

It is defined as the number of moles of solute dissolved in one litre or one cubic decimetre of the solution. It is a function of temperature.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in litre)}}$$

Molarity varies with temperature due to change in volume of solution.

Unit of molarity = g-mol/L

e.g. 0.25 mol L^{-1} (or 0.25 M) solution of NaOH means that 0.25 mol (or 10 g) of NaOH has been dissolved in one litre (or one cubic decimetre).

EXAMPLE |5| Calculate the molarity of each of the following solutions.

(i) 30 g of $Co(NO_3)_2 \cdot 6H_2O$ in 4.3 L of solution.

(ii) 30 mL of 0.5 M H_2SO_4 diluted to 500 mL. **NCERT Intext**

Sol. (i) Molecular mass of $Co(NO_3)_2 \cdot 6H_2O$

$= 58.7 + 2\times(14 + 3\times 16) + 6\times(2\times 1 + 16)$

$= 58.7 + 124 + 108 = 290.7\text{ g mol}^{-1}$

Number of moles of $Co(NO_3)_2 \cdot 6H_2O$

$$= \frac{\text{Mass of solute}}{\text{Molecular mass}}$$

$$= \frac{30}{290.7} = 0.103\text{ mol}$$

$$\text{Molarity of solution} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}}$$

$$= \frac{0.103}{4.3} = 0.024\text{ M}$$

(ii) (a) **First method**

$\because$ 1000 mL of 0.5 M H_2SO_4 will contain H_2SO_4 = 0.5 mol

$\therefore$ 30 mL of 0.5 M H_2SO_4 will contain H_2SO_4

$$= \frac{0.5}{1000}\times 30 = 0.015\text{ mol}$$

$$\text{Molarity of solution} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}}$$

$$= \frac{0.015}{0.500} = 0.03\text{ M}$$

(b) **Second method**

$$M_1V_1 = M_2V_2$$

$$0.5\times 30 = M_2\times 500$$

$$M_2 = 0.03\text{M}$$

Molality (*m*)

It is defined as the number of moles of solute per kilogram of the solvent.

Molality is independent of temperature.

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

e.g. 1.00 mol kg^{-1} (or 1.00 m) solution of KCl means that 1 mole (74.5 g) of KCl is dissolved in 1 kg of water.

EXAMPLE |6| If the density of some lake water is 1.25 g mL^{-1} and it contains 92 g of Na^+ ions per kg of water. Calculate the molality of Na^+ ions in the lake.

Foreign 2012, 2008; NCERT

Sol. Number of moles in 92 g of Na^+ ions

$$= \frac{\text{Mass}}{\text{Molecular mass}} = \frac{92}{23} = 4\text{ mol}$$

$$\text{Molality of } Na^+ \text{ ions} = \frac{\text{Number of moles}}{\text{Mass of solvent (kg)}}$$

$$= \frac{4}{1} = 4\text{ mol kg}^{-1}$$

TOPIC PRACTICE 1

OBJECTIVE Type Questions

1. Identify the phase of solute and solvent among the options are given below, for a solution as amalgam of mercury with sodium.

	Solute	Solvent
(a)	Solid	Liquid
(b)	Solid	Solid
(c)	Liquid	Solid
(d)	Solid	Gas

2. Which of the following is the correct example of solid solution in which the solute is in gas phase?
(a) Copper dissolved in gold (b) Camphor in nitrogen gas
(c) Hydrogen in palladium (d) All of these

3. 18 g of sucrose is dissolved in 162 g of water. Calculate the mass percentage of solution.
(a) 18 % (b) 10% (c) 20% (d) 15%

4. 184 g ethyl alcohol is mixed with 72 g of water. The ratio of mole fraction of alcohol to water is
(a) 3 : 4 (b) 1 : 2 (c) 1 : 4 (d) 1 : 1

5. Molarity (in mol/L) of distilled or pure water is
(a) 55.56 (b) 18 (c) 49.87 (d) 81

6. If 0.1 M $AgNO_3$ and 0.1 M NaCl solutions are mixed in same volume, then what will be the concentration of nitrate ions?
(a) 0.1 M (b) 0.2 M (c) 0.05 M (d) 0.025 M

7. What will be the concentration of 0.2M H_2SO_4 solution in g/L ?
(a) 21.4 (b) 39.2 (c) 9.8 (d) 19.6

8. 4 L of 0.02 M aqueous solution of NaCl was diluted by adding 1 L of water. The molarity of the resultant solution is .... **NCERT Exemplar**
(a) 0.004 (b) 0.008 (c) 0.012 (d) 0.016

9. The molality of a urea solution in which 0.0100 g of urea, $[(NH_2)_2CO]$ is added to 0.3000 dm^3 of water at STP is
(a) 0.555 m (b) 5.55×10^{-4} m
(c) 33.3 m (d) 3.33×10^{-2} m

10. Molality of an aqueous solution of urea is 4.44 mol/kg. In solution mole fraction of urea is
(a) 0.074 (b) 0.00133 (c) 0.008 (d) 0.0044

VERY SHORT ANSWER Type Questions

11. Give an example of a liquid solution in which the solute is a gas. **NCERT**

12. Define the term mass percentage. **NCERT**

13. Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN), when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN. **NCERT**

14. Define the term mole fraction. **All India 2012, 10, 09 C; Delhi 2012; NCERT**

15. State the main advantage of molality over molarity as the unit of concentration. **Delhi 2010, 2009C**

Or How does a change of temperature influence the values of molarity and molality of a solution? **Delhi 2011, 2009; Foreign 2011, 2009**

SHORT ANSWER Type I Questions

16. Will the molarity of a solution at 50°C be same, less or more than at 25°C?

17. A sugar syrup of weight 214.2 g contains 34.2 g of sugar ($C_{12}H_{22}O_{11}$). Calculate
(i) mole fraction of sugar
(ii) molality of sugar syrup

18. What volume of 95% sulphuric acid (density $= 1.85\ g/cm^3$) and what mass of water must be taken to prepare 100 cm^3 of 15% solution of sulphuric acid (density $= 1.10\ g/cm^3$)?

19. Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0.15 M solution in methanol. **NCERT**

20. Calculate the mass of urea (NH_2CONH_2) required in making 2.5 kg of 0.25 molal aqueous solution. **NCERT Intext**

SHORT ANSWER Type II Questions

21. Define the term solution. How many types of solutions are formed? Write briefly about each type with an example. **NCERT**

22. Concentrated nitric acid used in the laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid, if the density of the solution is 1.504 g mL^{-1}? NCERT

23. Calculate (i) molality (ii) molarity and (iii) mole fraction of KI if the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1}. NCERT

(i) As density and mass % is given, so find the mass of solute and solvent (as x% solution contains xg solute in $(100 - x)$ g solvent).
(ii) Find the volume of the solution, using the relation
$$\text{Volume} = \frac{\text{Mass}}{\text{Density}}$$
(iii) Recall the formulae of molality, molarity and mole fraction to calculate them.

24. (i) Calculate the molarity of a solution containing 4.9 g of H_2SO_4 in 500 cm^3 of the solution.
(ii) A solution contains 25% water, 25% ethanol and 50% acetic acid by mass. Calculate the mole fraction of each component.

25. A solution of glucose in water is labelled as 10% w/w. What would be the molality and mole fraction of each component in the solution? If the density of the solution is 1.2 g mL^{-1}, then what shall be the molarity of the solution? Delhi 2014; All India 2013; NCERT

26. (i) Define the following terms:
(a) molarity (b) molality,
Delhi 2014; All India 2009; NCERT
(ii) What is the molality of a urea solution in which 0.0100 g of urea $[(NH_2)_2CO]$ is added to 0.3000 dm^3 of water at STP?

LONG ANSWER Type Questions

27. (i) A sample of drinking water was found to be severely contaminated with chloroform ($CHCl_3$), supposed to be carcinogen. The level of contamination was 15 ppm (by mass).
(a) Express this in per cent by mass.
(b) Determine the molality of chloroform in the water sample. NCERT
(ii) An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1}, then what shall be the molarity of the solution? NCERT

28. How many mL of 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of both? NCERT

HINTS AND EXPLANATIONS

1. (*c*) In the amalgam of mercury with sodium, sodium metal is the solvent and mercury (which is a liquid) is solute.

2. (*c*) Solution of hydrogen in palladium is an example of solid solution in which solute is a gas. It is one of the rare examples in which solute is present in larger volume as compared to the solvent.

3. (*b*) We know that mass percentage
$$= \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100$$
and total mass of solution
$$= \text{mass of sucrose (solute)} + \text{mass of solvent (water)}$$
$$= (18 + 162)\text{g} = 180\text{ g}$$
$$\therefore \text{Mass percentage} = \frac{18}{180} \times 100 = 10\%$$

4. (*d*) Number of moles of $C_2H_5OH = \frac{184}{46} = 4;$
$(M_{C_2H_5OH} = 46 \text{ g/mol})$
Number of moles of $H_2O = \frac{72}{18} = 4;\quad (M_{H_2O} = 18 \text{ g/mol})$
$$\text{Mole fraction, } x_{C_2H_5OH} = \frac{4}{4+4} = \frac{4}{8}$$
$$x_{H_2O} = \frac{4}{4+4} = \frac{4}{8} \Rightarrow \frac{x_{C_2H_5OH}}{x_{H_2O}} = \frac{4/8}{4/8} = \frac{1}{1} = 1:1$$

5. (*a*) $$\text{Molarity of water} = \frac{\dfrac{\text{weight of water}}{\text{molecular weight of water}}}{\text{volume of water (in L)}}$$
Weight of water = density × volume (mL)
$= 1 \times 1000 = 1000$ g
Molecular weight of $(H_2O) = 2 \times 1 + 16 = 18$
$$\therefore \text{Molarity of water} = \frac{1000/18}{1} = 55.56 \text{ mol/L}$$

6. (*c*) Molarity (concentration) of nitrate ions
$$= \frac{\text{number of moles of nitrate ions}}{\text{total volume (in L)}}$$
$$= \frac{0.1\,V}{V+V} = \frac{0.1}{2} = 0.05 \text{ M} \quad [\because \text{same volume} = V]$$

7. (*d*) Molarity of H_2SO_4 solution = 0.2 mol/litre
Concentration of solution
= molarity of solution × molecular weight of matter
Molecular weight of H_2SO_4 = 98 g/mol
So, concentration of H_2SO_4 solution = $0.2 \times 98 = 19.6$ g/L.

8. (*d*) Given, $M_1 = 0.02$ M, $V_1 = 4$ L, $M_2 = ?$,
$V_2 = 4\text{ L} + 1\text{ L} = 5\text{ L}$
As we know, $M_1V_1 = M_2V_2$
$$0.02 \times 4\text{ L} = M_2 \times 5\text{L}$$
$$M_2 = \frac{0.08}{5} = 0.016\text{ M}$$

9. (*b*) Molality = $\frac{\text{Moles of solute}}{\text{Mass of water (in kg)}}$
Moles of urea = $\frac{0.010}{60}$ mol
Mass of water at STP $\quad (\because d = 1\text{g/cm}^3 = 1\text{kg/dm}^3)$
$$\text{Mass} = \frac{1\text{ kg}}{\text{dm}^3} \times 0.3\text{ dm}^3 = 0.3\text{ kg}$$
$$\therefore \quad \text{Molality} = \frac{0.010}{60 \times 0.3} = 5.55 \times 10^{-4}\text{ molal}$$

10. (*a*) 4.44 mol/kg means that, 4.44 moles of solute is present in 1 kg solvent (water).
Mole fraction of urea
$$= \frac{\text{number of moles of urea}}{\text{total number of moles present in solution}}$$
Number of moles of urea = 4.44
Number of moles of water = $\frac{1000}{18} = 55.56$
$$\therefore \text{ Mole fraction of urea} = \frac{4.44}{4.44 + 55.56} = 0.074$$

11. Solution of oxygen in water, aerated drinks etc.

12. The mass percentage of a component in a given solution is the mass of the component per 100 g of the solution

13. Mass percentage of aspirin = $\frac{\text{Mass of aspirin}}{\text{Mass of solutions}}$
$$= \frac{6.5\text{ g}}{(450 + 6.5)\text{ g}} = 1.424\%.$$

14. The ratio of number of moles of one component to the total number of moles of all the components present in the solution is called mole fraction.

15. Molality does not change with change in temperature while molarity decreases with rise in temperature.

16. Molarity at 50°C will be less than that at 25°C, because molarity decreases with increase in temperature.
Since, volume of the solution increases with increase in temperature but number of moles of solute remains the same.

17. Refer to Example 4 on page 4. [**Ans** 0.0099]
Refer to Example 6 on page 4. [**Ans** 0.56 m]

18. Refer to text on page 3.
[Ans: Volume of H_2SO_4 = 9.4 mL, mass of water = 90.6 g]

19. 0.15 M solution means 0.15 mole of benzoic acid are present in 1 L or 1000 mL of solution.
Molar mass of benzoic acid (C_6H_5COOH)
$= 6 \times 12 + 5 \times 1 + 1 \times 12 + 2 \times 16 + 1 = 122\text{ g mol}^{-1}$
$\because$ 1 mole of benzoic acid = 122 g
$\therefore$ 0.15 mole of benzoic acid = $0.15 \times 122 = 18.3$ g
$\because$ 0.15 mole are present in 1000 mL of solution.
So, 1000 mL of solution contains benzoic acid = 18.3 g
$\therefore$ 250 mL of solution contains benzoic acid
$$= \frac{18.3 \times 250}{1000} = 4.575\text{ g}$$

20. Since, the molal aqueous solution of urea is 0.25 m.
$\therefore$ Moles of urea = 0.25 mol
Mass of solvent (water) = 1 kg = 1000 g
Molar mass of urea (NH_2CONH_2)
$= 14 + 2 + 12 + 16 + 14 + 2 = 60\text{ g mol}^{-1}$
$\therefore$ 0.25 mole of urea = $0.25\text{ mol} \times 60\text{ g mol}^{-1} = 15$ g
Total mass of solution = 1000 g + 15 g
= 1015 g = 1.015 kg
Thus, 1.015 kg of solution contains urea = 15 g
$\therefore$ 2.5 kg of solution will require urea
$$= \frac{15\text{ g}}{1.015\text{ kg}} \times 2.5\text{ kg} = 37\text{ g}$$

21. Refer to text on pages 1 and 2.

22. 68% nitric acid by mass means that
Mass of nitric acid = 68 g
and Mass of solution = 100 g
Molar mass of HNO_3 = $1 + 14 + 3 \times 16 = 63\text{ g mol}^{-1}$
$\therefore$ Number of moles of 68 g HNO_3 = $\frac{68}{63}$ mol = 1.079 mol
$\because$ Density of solution = 1.504 g mL^{-1}
$\therefore$ Volume of solution = $\frac{100}{1.504}$ mL = 66.5 mL
= 0.0665 L
Thus, the molarity of the solution
$$= \frac{\text{Moles of the solute}}{\text{Volume of solution (in L)}}$$
$$= \frac{1.079}{0.0665}\text{ M} = 16.23\text{ M}$$

23. (a) **Molality** (*m*)
Weight of KI in 100 g of water = 20 g
Weight of water in the solution
= (100 − 20) g = 80 g = 0.08 kg
Molar mass of KI = 39 + 127 = 166 g mol^{-1}
Molality of the solution
$$(m) = \frac{\text{Number of moles of KI}}{\text{Mass of water (in kg)}} = \frac{(20\text{ g})/(166\text{ g mol}^{-1})}{(0.08\text{ kg})}$$
$$= 1.506\text{ mol kg}^{-1} = 1.506\text{ m}$$

(b) **Molarity (M)**

Weight of the solution = 100 g

Density of the solution = 1.202 g mL^{-1}

Volume of the solution = $\frac{\text{Weight of solution}}{\text{Density}}$

$$= \frac{(100 \text{ g})}{(1.202 \text{ g mL}^{-1})} = 83.19 \text{ mL} = 0.083 \text{ L}$$

Molarity of the solution (M)

$$= \frac{\text{Number of gram moles of KI}}{\text{Volume of solution in litres}}$$

$$= \frac{(20 \text{ g})/(166 \text{ g mol}^{-1})}{(0.083 \text{ L})}$$

$= 1.45 \text{ mol L}^{-1} = 1.45$ M

(c) **Mole fraction of KI**

Number of moles of KI,

$$n_{KI} = \frac{\text{Mass of KI}}{\text{Molar mass of KI}} = \frac{20 \text{ g}}{166 \text{ g mol}^{-1}} = 0.12 \text{ mol}$$

Number of moles of water

$$n_{H_2O} = \frac{\text{Mass of water}}{\text{Molar mass of water}} = \frac{80 \text{ g}}{18 \text{ g mol}^{-1}} = 4.44 \text{ mol}$$

Mole fraction of KI

$$\chi_{KI} = \frac{n_{KI}}{n_{KI} + n_{H_2O}} = \frac{(0.12 \text{ mol})}{(0.12 + 4.44) \text{ mol}}$$

$$= \frac{0.12}{4.56} = 0.0263$$

24. (i) Refer to Example 5(i) on page 4. [Ans 0.1 m]

(ii) Refer to Example 4 on page 4.

[Ans Mole fraction of water = 0.583

Mole fraction of C_2H_5OH = 0.196

Mole fraction of CH_3COOH = 0.301]

25. 10 g glucose is present in 100 g solution, i.e. there is 90 g of water = 0.090 kg of water

Number of moles of 10 g glucose = $\frac{10}{180}$ mol = 0.0555 mol

Number of moles of 90 g H_2O = $\frac{90}{18}$ = 5 mol

Molality of glucose = $\frac{0.0555 \text{ mol}}{0.090 \text{ kg}}$ = 0.617 m

Mole fraction of glucose, $\chi_{glucose} = \frac{0.0555}{5 + 0.0555} = 0.01$

$\chi_{(H_2O)} = 1 - 0.01 = 0.99$

$\because$ The density of solution = 1.2 g mL^{-1} (Given)

$\therefore$ Volume of 100 g solution = $\frac{100}{1.2}$ mL

= 83.33 mL = 0.08333 L

Thus, molarity = $\frac{0.0555 \text{ mol}}{0.08333 \text{ L}}$ = 0.67 M

26. (i) (a) Refer to text on page 4.

(b) Refer to text on page 4.

(ii) Refer to sol 9 on page 7.

27. (i) (a) 15 ppm means 15 parts in million (10^6) parts by mass in the solution.

Therefore, % by mass = $\frac{15}{10^6} \times 100$

$= 15 \times 10^{-4} = 1.5 \times 10^{-3}\%$

(b) Taking 15 g chloroform in 10^6 g of the solution, mass of solvent $\approx 10^6$ g

Molar mass of $CHCl_3$ = 12 + 1 + 3 × 35.5

= 119.5 g mol^{-1}

$$\therefore \text{Molality} = \frac{\text{Mass of CHCl}_3 / \text{Molar mass}}{\text{Mass of water (in kg)}}$$

$$= \frac{15/119.5}{10^6} \times 1000 = 1.25 \times 10^{-4} \text{ m}$$

(ii) Mass of ethylene glycol = 222.6 g

Molar mass of ethylene glycol ($C_2H_6O_2$)

$= (12 \times 2) + (1 \times 6) + (16 \times 2) = 24 + 6 + 32 = 62$ g mol^{-1}

Mass of water = 200 g = 0.2 kg

$$\text{Molality } (m) = \frac{\text{Mass of ethylene glycol / Molar mass}}{\text{Mass of solvent in kg}}$$

$$= \frac{(222.6 \text{ g}) / (62 \text{ g mol}^{-1})}{0.2 \text{ kg}} = 17.95 \text{ mol kg}^{-1} = 17.95 \text{ m}$$

Density of the solution = 1.072 g mL^{-1}

Mass of solution = Mass of solute + Mass of solvent

= 222.6 g + 200 g = 422.6 g

$$\text{Volume} = \frac{\text{Mass}}{\text{Density}} = \frac{422.6 \text{ g}}{1.072 \text{ g mL}^{-1}} = 394.2 \text{ mL}$$

$$\text{Molarity } (M) = \frac{\text{Mass of ethylene glycol / Molar mass}}{\text{Volume in litres}}$$

$$= \frac{(222.6 \text{ g}) / (62 \text{ g mol}^{-1})}{0.3942 \text{ L}} = 9.10 \text{ mol L}^{-1} = 9.10 \text{ M}$$

28. Suppose, amount of Na_2CO_3 present in the mixture = x g

$\therefore$ $NaHCO_3$ present in the mixture = $(1 - x)$ g

Molar mass of Na_2CO_3 = 2 × 23 + 12 + 3 × 16 = 106 g mol^{-1}

Molar mass of $NaHCO_3$ = 23 + 1 + 12 + 3 × 16 = 84 g mol^{-1}

$\therefore$ Moles of Na_2CO_3 in x g = $\frac{x}{106}$ and

Moles of $NaHCO_3$ in $(1 - x)$ g = $\frac{1 - x}{84}$

As mixture contains equimolar amounts of the two,

$$\therefore \quad \frac{x}{106} = \frac{1 - x}{84}$$

or $106 - 106x = 84x$ or $x = \frac{106}{190}$ g = 0.558 g

Thus, number of moles of $Na_2CO_3 = \frac{0.558}{106} = 0.00526$ mol

and number of moles of $NaHCO_3 = \frac{1-0.558}{84}$

$= \frac{0.442}{84} = 0.00526$ mol

Again by reactions,

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

$\because$ 1 mole of Na_2CO_3 requires HCl = 2 mol

$\therefore$ 0.00526 mole of Na_2CO_3 requires HCl

$= 0.00526 \times 2$ mol $= 0.01052$ mol

$\because$ 1 mole of $NaHCO_3$ requires HCl = 1 mol

$\therefore$ 0.00526 mole of $NaHCO_3$ requires HCl = 0.00526 mol

$\therefore$ Total HCl required = (0.01052 + 0.00526) mol

= 0.01578 mol

Again, 0.1 mole of 0.1 M HCl is present in 1000 mL of HCl.

$\therefore$ 0.01578 mole of 0.1 M HCl will be present in HCl

$= \frac{1000}{0.1} \times 0.01578 = 157.8$ mL

|TOPIC 2| Solubility

Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent under specified conditions.

It depends on

(i) nature of solute (ii) nature of solvent
(iii) temperature (iv) pressure

SOLUBILITY OF A SOLID IN A LIQUID

Solids are soluble in a liquid if their intermolecular interactions are similar. The solubility of a solid in a liquid at any temperature is defined as the maximum amount of the solid (solute) in gram which can be dissolved in 100 g of the liquid (solvent) to form the saturated solution at that particular temperature.

Terms Related to Solubility of a Solid in a Liquid

The terms which are needed to understand the solubility of a solid in a liquid are given below:

(i) **Dissolution** When a solid solute is added to the solvent, some solute dissolves and its concentration increases in the solution, this process is known as dissolution.

(ii) **Crystallisation** Some solute particles in solution combine with each other and get separated out of solution. This process is known as crystallisation.

(iii) **Dynamic equilibrium** It is the condition, when number of solute particles going into solutions is equal to the solute particles separating out, i.e. dissolution and crystallisation processes occurring at the same rate.

$$\text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution}$$

At this stage, the concentration of solute in solution will remain constant under the given conditions, i.e. temperature and pressure. Similar process is followed when gases are dissolved in liquid solvents.

(iv) **Saturated solution** The process of dissolution continues until the solution attains a certain maximum concentration.Such a solution in which no more solute can be dissolved at the same temperature and pressure, is known as saturated solution.

In saturated solution, a dynamic equilibrium gets established between the process of dissolution and crystallisation.

$$\text{Solute} + \text{Solvent} \underset{\text{Crystallisation}}{\overset{\text{Dissolution}}{\rightleftharpoons}} \text{Solution}$$

(v) **Unsaturated solution** An unsaturated solution is one in which more solute can be dissolved without changing the temperature.

Process of Solubility of a Solid in a Liquid

Complete process for the solubility of solid in a liquid is discussed below:

When a solid solute is added continuously in a solvent, the solute keeps on dissolving and the concentration of the solution increases (dissolution). Some solute particles in a solution get separated out of the solution (crystallisation). A stage is reached when the dissolution and crystallisation processes occur at the same rate.

At this stage, number of solute particles going into the solution will be equal to the solute particles separating out and it can be called that a state of dynamic equilibrium has been achieved. At equilibrium, no more solute can be dissolved hence, a saturated solution is obtained at the given conditions of temperature and pressure. Thus, the concentration of solute in such a solution is its solubility.

Factors Affecting the Solubility of a Solid in a Liquid

These are given below:

(i) **Nature of solute and solvent** This can be understood by saying "***like dissolves like***". It means that polar or ionic compounds (like NaCl) dissolve in polar solvents (like water) and almost insoluble in non-polar solvents (like benzene). Similarly, non-polar (i.e. covalent or organic) compounds (like naphthalene, anthracene) are soluble in non-polar solvents (like benzene, ether) and are less soluble in polar solvents (like water). Solubility in general, is result of three kinds of inter-particles interactions, i.e. solute-solute, solute-solvent and solvent-solvent interactions.

(ii) **Effect of temperature** The solubility of a solid in a liquid is significantly affected by temperature change.

In general, if in a nearly saturated solution, the dissolution process is endothermic, i.e. $\Delta_{sol} H > 0$, the solubility should increase with the rise in temperature and if it is exothermic, i.e. $\Delta_{sol} H < 0$, the solubility should decrease in accordance with **Le-Chatelier's principle**. This can be also observed experimentally.

Note Pressure does not have any significant effect on solubility of solids in liquids because solids and liquids are highly incompressible and practically remain unaffected by the pressure change.

SOLUBILITY OF A GAS IN A LIQUID

Almost all gases are soluble in water though to different extents. The solubility of any gas in a particular liquid is the volume of the gas (in cubic centimetre, cc) that can be dissolved in unit volume (1cc) of the liquid to form the saturated solution at certain temperature and under a pressure of one atmosphere.

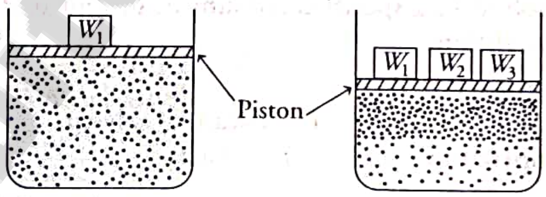
Factors Affecting the Solubility of a Gas in a Liquid

These are as follows:

(i) **Nature of gas** (solute) **and liquid** (solvent)
The solubility of different gases in the same solvent varies, e.g. gases like hydrogen, oxygen, nitrogen and helium, etc., dissolve in water to a small extent whereas the gases like NH_3, HCl, SO_2, etc., are highly soluble in water.

(ii) **Effect of temperature** The solubility of a gas decreases with increase in temperature. This is because when a gaseous solution is heated, the molecular motion of gaseous particles increases, as a result some molecules escape out of the solution. Also, the dissolution of a gas in a liquid is an exothermic process, so heat is evolved. So, applying Le-Chatelier's principle, with the increase of temperature, the solubility should decrease.
(As gas + solvent $\rightleftharpoons$ solution + heat, equilibrium shifts towards backward direction).

(iii) **Effect of pressure** The solubility of a gas increases with increase in pressure. In this method, the gas is compressed over the liquid under the high pressure. Hence, the solubility increases.
For the solution of gases in a solvent, consider a system as shown below :



Effect of pressure on the solubility of a gas. The concentration of dissolved gas is proportional to the pressure applied above the solution

The lower part is solution and the upper part is gaseous system at pressure p and temperature T. Assume this system to be in a state of dynamic equilibrium, i.e. under these conditions, rate of gaseous particles entering and leaving the solution phase is the same. On increasing the pressure over the solution phase by compressing the gas to a smaller volume, there is an increase in the number of gaseous particles per unit volume over the solution and also the rate at which the gaseous particles are striking the surface of solution to enter it. The solubility of the gas will increase until a new equilibrium is reached resulting in an increase in the pressure of the gas above the solution and thus, its solubility increases. In order to explain the effect of pressure on solubility of gas, Henry derived a relation, which is discussed here.

Henry's Law

Henry was the first one to give a quantitative relation between pressure and solubility of a gas in a solvent which is called Henry's law. It states that *at a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.*
Dalton, a contemporary of Henry, independently concluded that if we use the mole fraction of a gas in the solution as a measure of its solubility, then it can be said that, *the mole fraction of the gas (χ) in the solution is proportional to the partial pressure of the gas (p) over the solution.*

The most common forms of Henry's law states that, *the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (χ) in the solution.* It is expressed as

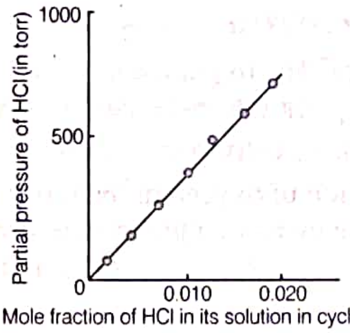
$$p \propto \chi \quad \text{or} \quad \boxed{p = K_H \cdot \chi} \qquad \text{...(i)}$$

where, K_H is called Henry's law constant.

Hence, $$K_H = \frac{1}{K'}$$

Graphical Representation to Validate Henry's Law

If we draw a graph between the partial pressure of the gas against the mole fraction of the gas in solution at a given temperature, then a straight line passing through the origin is obtained as shown in the figure given below.



Experimental results for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's law constant, K_H

Henry's law is applied to each gas independent of the presence of other gases.

Note

Different gases have different K_H values at the same temperature which suggests that K_H is a function of the nature of the gas.

EXAMPLE |1| H_2S, a toxic gas with rotten egg like smell, is used for qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant. **NCERT Intext**

Sol. Solubility of H_2S gas = 0.195 m, i.e. 0.195 moles in 1 kg of the solvent (water)

∵ Number of moles of H_2O in 1 kg of the solvent (water)

$$= \frac{1000 \text{ g}}{18 \text{ g mol}^{-1}} = 55.55 \text{ mol}$$

∴ Mole fraction of H_2S gas in the solution

$$(\chi) = \frac{0.195}{0.195 + 55.55} = \frac{0.195}{55.745} = 0.0035$$

Pressure at STP = 0.987 bar

According to Henry's law, $p_{H_2S} = K_H \times \chi_{H_2S}$

or $$K_H = \frac{p_{H_2S}}{\chi_{H_2S}} = \frac{0.987 \text{ bar}}{0.0035} = 282 \text{ bar}$$

Significance of Henry's Law

From the Eq. (i), it can be concluded that higher the value of K_H at a particular pressure, the lower is the solubility of the gas in the liquid.

K_H values for both N_2 and O_2 increase with increase of temperature indicating that the solubility of gas in liquid decreases with increase of temperature. It is due to this reason that aquatic species are more comfortable in cold water rather than in warm water.

EXAMPLE |2| At same temperature, H_2 is more soluble in water than He. Which of them has higher value of K_H and why?

Sol. He has higher value of K_H because if the gas has more solubility, its K_H value will be low.

Applications of Henry's Law

Henry's law finds several applications in industries. It also explains many biological phenomena.

These are as follows:

(i) **In the production of carbonated beverages** To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

(ii) **In deep sea diving** Scuba divers (deep-sea divers) breath air at high pressure under water. Increased pressure increases the solubility of atmospheric gases (like nitrogen) in blood. When divers come towards surface, the pressure gradually decreases resulting in the release of dissolved gases from blood. This leads to the formation of bubbles of nitrogen in the blood, which blocks capillaries and gives rise to an ailment called **bends or decompression sickness.**

To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

(iii) **For people living at high altitudes or climbers** At high altitudes, the partial pressure of oxygen is less than that at the ground level. This leads to low concentration of oxygen in the blood and tissues of people living at high altitudes or climbers. Consequently, they feel weak both physically and mentally. These are the symptoms of a medical condition known as anoxia.

Limitations of Henry's Law

It is applicable only when

(i) the pressure of the gas is not too high and temperature is not too low.

(ii) the gas should not undergo any chemical change.

(iii) the gas should not undergo association or dissociation in the solution.

TOPIC PRACTICE 2

OBJECTIVE Type Questions

1. On dissolving sugar in water at room temperature, solution feels cool to touch. Under which of the following cases dissolution of sugar will be most rapid? **NCERT Exemplar**
(a) Sugar crystals in cold water
(b) Sugar crystals in hot water
(c) Powdered sugar in cold water
(d) Powdered sugar in hot water

2. Solubility of gases in liquids decreases with rise in temperature because dissolution is an **CBSE SQP (Term I)**
(a) endothermic and reversible process
(b) exothermic and reversible process
(c) endothermic and irreversible process
(d) exothermic and irreversible process

3. A beaker contains a solution of substance '*A*'. Precipitation of substance '*A*' takes place when small amount of '*A*' is added to the solution. The solution is .... **NCERT Exemplar**
(a) saturated (b) supersaturated
(c) unsaturated (d) concentrated

4. Maximum amount of a solid solute that can be dissolved in a specified amount of a given liquid solvent does not depend upon ....
(a) temperature (b) nature of solute
(c) pressure (d) nature of solvent

5. Pressure does not have any significant effect on solubility of solids in liquids because **CBSE 2021 (Term I)**
(a) solids are highly compressible
(b) liquids are highly compressible
(c) solubility of solid in liquid is directly proportional to partial pressure
(d) solids and liquids are highly incompressible

6. Which of the following units is useful in relating concentration of solution with its vapour pressure? **NCERT Exemplar**
(a) Mole fraction (b) Parts per million
(c) Mass percentage (d) Molality

7. Value of Henry's constant K_H ..... . **NCERT Exemplar**
(a) increases with increase in temperature
(b) decreases with increase in temperature
(c) remains constant
(d) first increases then decreases

8. In the graph given below, what does the slope of the line represent?

(a) Partial pressure of the gas in vapour phase (p)
(b) Mole fraction of gas in the solution (χ)
(c) Henry's law constant (K_H)
(d) All of the above

9. K_H value for Ar(*g*), CO_2 (*g*), HCHO (*g*) and CH_4(*g*) are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively. Arrange these gases in the order of their increasing solubility. **NCERT Exemplar**
(a) HCHO < CH_4 < CO_2 < Ar
(b) HCHO < CO_2 < CH_4 < Ar
(c) Ar < CO_2 < CH_4 < HCHO
(d) Ar < CH_4 < CO_2 < HCHO

10. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to .... **NCERT Exemplar**
(a) low temperature
(b) low atmospheric pressure
(c) high atmospheric pressure
(d) Both low temperature and high atmospheric pressure

VERY SHORT ANSWER Type Questions

11. Name the four important factors on which solubility depends.

12. Why do smaller particles dissolve faster than larger ones?

13. $\Delta_{sol}H$ of NH_4Cl is > 0. What is the effect of temperature on its solubility?

14. Why do gases always tend to be less soluble in liquid as the temperature is raised? **NCERT**

15. The K_H value for H_2 in water is 71.18 k bar but its value changes to 3. 67 k bar when the solvent is benzene. Why?

SHORT ANSWER Type I Questions

16. Give reasons for the following
(a) Aquatic species are more comfortable in cold water than warm water.
(b) At higher altitudes people suffer from anoxia resulting in inability to think. **All India 2019**

17. Based on solute-solvent interactions, arrange the following in the increasing order of solubility in n-octane and explain.
Cyclohexane, KCl, CH_3OH, CH_3CN NCERT

18. State Henry's law. What is the effect of temperature on the solubility of a gas in a liquid? All India 2012; 2014

19. What is the significance of Henry's law constant K_H? NCERT Exemplar

SHORT ANSWER Type II Questions

20. Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?
(i) Phenol (ii) Toluene
(iii) Formic acid (iv) Ethylene glycol
(v) Chloroform (vi) Pentanol NCERT

21. Suggest the most important type of intermolecular interaction in the following pairs.
(i) n-hexane and n-octane
(ii) I_2 and CCl_4 (iii) $NaClO_4$ and water
(iv) Methanol and acetone
(v) Acetonitrile (CH_3CN) and acetone (C_3H_6O)
(vi) Water and alcohol NCERT

22. The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 K, respectively. The water is in equilibrium with air at a pressure of 10 atm. At 298 K, if the Henry's law constant for oxygen and nitrogen are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water. NCERT

23. The partial pressure of ethane over a saturated solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution were to contains 5.0×10^{-2} g of ethane, then what will be the partial pressure of the gas? NCERT; Delhi 2013 C

LONG ANSWER Type Questions

24. What is the solubility of a solid in liquid? Describe the various factors on which the solubility of a solid in a liquid depends?

25. Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

26. (i) Henry's law constant for the molality of methane in benzene at 298 K is 4.27×10^5 mm of Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm of Hg. NCERT
(ii) The solubility of $Ba(OH)_2 \cdot 8H_2O$ in water is 5.6 g per 100 g of water at 288 K. Calculate the molality of hydroxide ion in saturated solution of $Ba(OH)_2 \cdot 8H_2O$ at that temperature.
(iii) Mention some important applications of Henry's law. NCERT

HINTS AND EXPLANATIONS

1. (*d*) Dissolution of sugar in water will be most rapid when powdered sugar is dissolved in hot water because powder form can easily insert in the vacancies of liquid particles.
Further dissolution of sugar in water is an endothermic process. Hence, high temperature will favour the dissolution of sugar in water.

2. (*b*) The dissolution of gas in a liquid is an exothermic process, so heat is evolved. According to Le-Chatelier's principle, solubility of gases in liquid decreases with increase in temperature and it is reversible process.

3. (*b*) When solute is added to the solution three cases may arise
(i) It it dissolves into solution then solution is unsaturated.
(ii) It it does not dissolve in the solution then solution is known as saturated.
(iii) When solute get precipitated, solution is known as supersaturated solution.

4. (*c*) Maximum amount of solid that can be dissolved in a specified amount of a given solvent does not depend upon pressure. This is because solid and liquid are highly incompressible and practically remain unaffected by change in pressure.

5. (*d*) Solids and liquids are highly incompressible. Hence, their solubility does not affected with changes in pressure.
However, solubility of gases in a liquid is directly proportional to the pressure of that gas above the surface of the solution.

6. (*a*) According to Henry's law, partial pressure of gas in the solution is proportional to the mole fraction of gas in the solution.

$$p = K_H x$$

where, K_H = Henry's constant
Hence, (a) mole fraction is the correct choice.

7. (*a*) Value of Henry's constant (K_H) increases with increase in temperature representing the decrease in solubility.

8. (*c*) On comparing $p = K_H \cdot x$ with equation of straight line *viz*

$y = mx, \therefore m = K_H$ (Here, m = slope of the line).

Thus, Henry's law constant is represented by the slope of the line.

9. (*c*) **Hint :** The value of K_H rises, solubility of gases decreases.

Hence, correct order is Ar < CO_2 < CH_4 < HCHO and correct choice is (c).

10. (*b*) Low concentration of oxygen in the blood and tissues of people living at high altitude is due to low atmospheric pressure.

Because at high altitude, the partial pressure of oxygen is less than at the ground level. This decreased atmospheric pressure causes release of oxygen from blood.

11. Solubility depends on

(i) nature of solute (ii) nature of solvent

(iii) temperature (iv) pressure

12. Particles with smaller size diffuse easily through the intermolecular spaces of solvent, hence they dissolve faster.

13. Since, this process is endothermic, the solubility increases with increase in temperature.

14. As dissolution of gas in liquid is an exothermic process (Gas + Solvent $\rightleftharpoons$ Solution + Heat). So, on increasing the temperature, equilibrium shifts towards the backward direction.

15. **Hint** Higher the value of K_H for a gas, lower will be its solubility and *vice-versa*.

Refer to text on pages 10 and 11.

16. (a) Aquatic species are more comfortable in cold water than warm water because amount of dissolved oxygen decreases with the rise in temperature (per unit area) in accordance with Henrys law. Hence species do not get sufficient oxygen.

(b) At higher altitude people suffer from anoxia because at higher altitudes, the partial pressure of oxygen is less than that at ground level. This leads to low concentration of oxygen in the blood and tissues of people.

17. (i) As cyclohexane and *n*-octane both are non-polar. Hence, they will mix completely in all proportions.

(ii) KCl is an ionic compound while *n*-octane is non-polar. Hence, KCl will not dissolve in *n*-octane.

(iii) CH_3OH and CH_3CN both are polar but CH_3CN is less polar than CH_3OH. As the solvent (*n*-octane) is non-polar, CH_3CN will dissolve more than CH_3OH in *n*-octane.

Therefore, the order of solubility will be

KCl < CH_3OH < CH_3CN < cyclohexane

18. Henry's law Refer to text on page 10.

Effect of temperature Solubility of gases decreases with increase in temperature.

19. Refer to text on page 11.

20. (i) **Phenol** Partially soluble (Reason: Phenol has polar — OH group and non-polar — C_6H_5 group).

(ii) **Toluene** Insoluble (Reason: Toluene is non-polar, water is polar.)

(iii) **Formic acid** Highly soluble (Reason: Hydrogen bonding).

(iv) **Ethylene glycol** Highly soluble (Reason: Hydrogen bonding).

(v) **Chloroform** Insoluble (Reason: H-bonds are formed although polarity is present).

(vi) **Pentanol** Partially soluble (Reason: — OH group is polar but long hydrocarbon part is non-polar).

21. (i) Since, both are non-polar. Hence, intermolecular interactions between them are **London dispersion forces.**

(ii) Same as (i).

(iii) Since, $NaClO_4$ gives Na^+ and ClO_4^- ions in the solution while water is a polar molecule. Hence, intermolecular interactions between them will be **ion-dipole** interactions.

(iv) As both are polar molecules. Hence, intermolecular interactions between them will be **dipole-dipole** interactions.

(v) Same as (iv).

(vi) Both are polar, they form H-bonds with each other.

22. Given that, total pressure of air in equilibrium with water = 10 atm

As air contains 20% oxygen and 79% nitrogen by volume.

$\therefore$ Partial pressure of oxygen

$$(p_{O_2}) = \frac{20}{100} \times 10 \text{ atm} = 2 \text{ atm} = 2 \times 760 \text{ mm} = 1520 \text{ mm}$$

Partial pressure of nitrogen, $(p_{N_2}) = \frac{79}{100} \times 10$ atm

$$= 7.9 \text{ atm} = 7.9 \times 760 \text{ mm} = 6004 \text{ mm}$$

Given that, $K_H(O_2) = 3.30 \times 10^7$ mm,

$K_H(N_2) = 6.51 \times 10^7$ mm

According to Henry's law,

$$p_{O_2} = K_H \times \chi_{O_2}$$

or $$\chi_{O_2} = \frac{p_{O_2}}{K_H} = \frac{1520 \text{ mm}}{3.30 \times 10^7 \text{ mm}} = 4.61 \times 10^{-5}$$

$$p_{N_2} = K_H \times \chi_{N_2}$$

or $$\chi_{N_2} = \frac{p_{N_2}}{K_H} = \frac{6004 \text{ mm}}{6.51 \times 10^7 \text{ mm}} = 9.22 \times 10^{-5}$$

23. According to Henry's law,

$$m \propto p \Rightarrow m = Kp$$

$$6.56 \times 10^{-3} \text{ g} = K \times 1 \text{ bar}$$

$$K = 6.56 \times 10^{-3} \text{ g bar}^{-1}$$

Again, when $m' = 5.00 \times 10^{-2}$ g, $p' = ?$

$$m' = K \times p'$$
$$5.00 \times 10^{-2}\ \text{g} = 6.56 \times 10^{-3}\ \text{g bar}^{-1} \times p'$$
$$p' = \frac{5.00 \times 10^{-2}}{6.56 \times 10^{-3}} = 7.62\ \text{bar}$$

24. Refer to text on pages 9 and 10.

25.

> To calculate the mass of CO_2 dissolved, calculate the mole fraction of CO_2 by using Henry's law,
> $$p = K_H \times \chi \quad \text{or} \quad \chi = \frac{p}{K_H}$$
> Then, calculate the number of moles and finally the mass.

***Step* I** Calculation of number of moles of CO_2

According to Henry's law,

$$\text{Mole fraction of } CO_2\ (\chi_{CO_2}) = \frac{\text{Partial pressure of } CO_2}{K_H \text{ for } CO_2}$$

$$K_H = 1.67 \times 10^8\ \text{Pa} = \frac{(1\ \text{atm})}{(101325\ \text{Pa})} \times (1.67 \times 10^8\ \text{Pa})$$
$$= 1.648 \times 10^3\ \text{atm}$$

$$\chi_{CO_2} = \frac{2.5\ \text{atm}}{(1.648 \times 10^3\ \text{atm})} = 1.52 \times 10^{-3}$$

$$n_{H_2O} = \frac{(500\ \text{g})}{(18\ \text{g mol}^{-1})} = 27.78\ \text{mol}$$

$$\chi_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} = \frac{n_{CO_2}}{n_{H_2O}} = \frac{n_{CO_2}}{(27.78\ \text{mol})}$$

$$n_{CO_2} = \chi_{CO_2} \times (27.78\ \text{mol})$$
$$= (1.52 \times 10^{-3}) \times (27.78\ \text{mol}) = 0.0422\ \text{mol}$$

Note n_{CO_2} is considered negligible due to its low solubility in water.

***Step* II** Calculation of mass of dissolved CO_2 in water

Mass of CO_2 = Number of moles of CO_2 × Molar mass of CO_2

$$= (0.0422\ \text{mol}) \times (44\ \text{g mol}^{-1}) = 1.857\ \text{g}$$

26. (i) According to Henry's law, $p = K_H \cdot \chi$

So, $$\chi = \frac{p}{K_H} = \frac{760}{4.27 \times 10^5} = 1.78 \times 10^{-3}$$

or the mole fraction of methane in benzene is 1.78×10^{-3}.

(ii) Molar mass of $Ba(OH)_2 \cdot 8H_2O = 137 + 2 \times 17 + 8 \times 18$
$$= 315\ \text{g mol}^{-1}$$

∴ 100 g water has 5.6 g of $Ba(OH)_2 \cdot 8H_2O$

∴ 1000 g water will have $Ba(OH)_2 \cdot 8H_2O = 56$ g

Number of moles of
$$Ba(OH)_2 \cdot 8H_2O = \frac{56}{315} = 0.178\ \text{mol}$$

Thus, molality of $Ba(OH)_2 = 0.178$ m

$$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$$

Molality of OH^- ions = 2 × molality of $Ba(OH)_2$
$$= 2 \times 0.178 = 0.356\ \text{m}$$

(iii) Refer to text on page 11 and 12.

|TOPIC 3|

Vapour Pressure of Liquid Solutions

VAPOUR PRESSURE

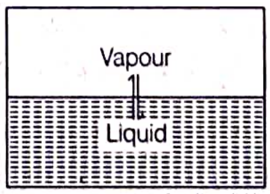
The pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature is called vapour pressure.

In simple terms, the pressure exerted by the vapour molecules on the surface of liquid in a jar at equilibrium is known as vapour pressure.

Vapour pressure is affected by the nature and temperature of the liquid. Weaker the intermolecular forces, greater is the amount of vapours because more molecules can leave the liquid and come into vapour phase.

Similarly, when the temperature is raised, the vapour pressure will also increase.

This is because with increase in temperature, kinetic energy of the molecules increases and hence, more molecules leave the surface of liquid and change into the vapour phase.



Vapour pressure of a liquid/gas

Liquid solutions are formed when solvent is a liquid. The solute can be a gas, a liquid or a solid. In the solutions of liquids and solids in a liquid, generally, the liquid solvent is volatile. The solute may or may not be volatile.

The solutions containing two components are:

(i) liquids in liquids (ii) solids in liquids

Vapour Pressure of Liquid-Liquid Solutions

In a binary solution of two volatile liquids in a closed vessel, both the components get evaporated and finally a state of equilibrium is established between the vapour and liquid phase. The total vapour pressure in this case is equal to the sum of the partial pressures of each of the two components (according to Dalton's law of partial pressure). These partial pressures are related to the mole fractions of the two components.

Relation between partial pressures and mole fraction was further explained by Raoult, which is discussed below :

Raoult's Law

The French chemist, **Francois Marte Raoult** (1886) gave a quantitative relationship between the partial pressures and the mole fractions of two components. This relationship is known as Raoult's law Thus, Raoult's law states that "*at a given temperature, for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution*".

Let us consider that two volatile liquids 1 and 2 have mole fractions as χ_1 and χ_2, respectively. If p_1 and p_2 are the vapour pressures of these components in the solution, respectively, at same temperature then according to Raoult's law,

For component 1, $p_1 \propto \chi_1$ or $p_1 = p_1^\circ \chi_1$

Similarly, for component 2, $p_2 = p_2^\circ \chi_2$

According to Dalton's law of partial pressure, the total pressure (p_{total}) over the solution phase in the container will be sum of the partial pressures of the components of the solution and is given as

$$p_{total} = p_1 + p_2$$

So, $p_{total} = p_1^\circ \chi_1 + p_2^\circ \chi_2$

As we know, $\chi_1 + \chi_2 = 1$ or $\chi_1 = 1 - \chi_2$,

Then, $p = p_1^\circ (1 - \chi_2) + p_2^\circ \chi_2$

$$\boxed{p = p_1^\circ + (p_2^\circ - p_1^\circ)\chi_2}$$

From this equation, following conclusions can be drawn:

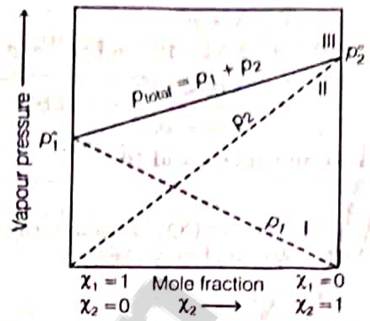
(i) The total vapour pressure over the solution can be related to the mole fraction of any one component.

(ii) Total vapour pressure over the solution varies linearly with the mole fraction of component 2.

(iii) The total vapour pressure over the solution increases or decreases with increase in mole fraction of component 1, depending upon the vapour pressures of the pure components 1 and 2.

Graphical Representation of Raoult's Law

A plot of p_1 and p_2 *versus* the mole fractions χ_1 and χ_2 for a solution gives a linear plot as shown in the given figure.



Plot of vapour pressure and mole fraction of an ideal solution at constant temperature

In the above figure, the dashed lines I and II represent the partial pressure of the components. (It can be seen from the plot that p_1 and p_2 are directly proportional to χ_1 and χ_2, respectively.) These lines (I and II) pass through the points for which χ_1 and χ_2 are equal to unity. The total vapour pressure is given by line marked III in the figure.

The plot (line III) of p_{total} *versus* χ_2 is a straight line as shown in figure.

Assuming that $p_1^\circ < p_2^\circ$ i.e. component 1 is less volatile than component 2, then the minimum value of p_{total} is p_1° and the maximum value is p_2°.

The composition of vapour phase in equilibrium with the solution can be determined by the partial pressures of the components. If y_1 and y_2 are the mole fractions of the components 1 and 2 respectively in the vapour phase then, using Dalton's law of partial pressure;

$$p_1 = y_1 p_{total}$$

$$p_2 = y_2 p_{total}$$

In general, for a solution containing a number of volatile components (liquids), for any component i,

$$p_i = y_i \cdot p_{total}$$

Raoult's Law as a Special Case of Henry's Law

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by

$$p_i = \chi_i p_i^\circ$$

If in the solution of a gas in a liquid, the volatile component exists as a gas then, according to Henry's law, $p = K_H \chi$, i.e. partial pressure of the volatile component (gas) is directly proportional to the mole fraction of that component (gas) in the solution.

Therefore, Raoult's and Henry's laws become identical except that their proportionality constants (K_H-Henry's constant and p_i° constant for Raoult's law) are different. Therefore, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_i°.

EXAMPLE |1| The vapour pressure of ethyl alcohol at 298 K is 20 mm of Hg. Its mole fraction in a solution with methyl alcohol is 0.40. What is its vapour pressure in solution if the mixture obeys Raoult's law?

Sol. According to Raoult's law,

$$p_A = p_A^\circ \chi_A$$

Vapour pressure of pure ethyl alcohol

$(p_A^\circ) = 20$ mm of Hg

Mole fraction of ethyl alcohol $(\chi_A) = 0.40$

Vapour pressure of ethyl alcohol in solution

$(p_A) = 20 \times 0.40 = 8$ mm of Hg

EXAMPLE |2| The vapour pressures of pure liquids *A* and *B* are 450 and 700 mm of Hg at 350 K, respectively. Find out the composition of the liquid mixture, if total vapour pressure is 600 mm of Hg. Also, find the composition of the vapour phase. **NCERT Intext**

Sol. Given, $p_A^\circ = 450$ mm of Hg, $p_B^\circ = 700$ mm of Hg

$p_{\text{total}} = 600$ mm of Hg

According to Raoult's law,

$$p_A = \chi_A \times p_A^\circ$$

$$p_B = \chi_B \times p_B^\circ = (1-\chi_A)\, p_B^\circ$$

$$p_{\text{total}} = p_A + p_B = \chi_A p_A^\circ + (1-\chi_A)\, p_B^\circ$$

$$= p_B^\circ + (p_A^\circ - p_B^\circ)\chi_A$$

On substituting the values, we get

$$600 = 700 + (450 - 700)\,\chi_A$$

or $\quad 250\chi_A = 100$

or $\quad \chi_A = \dfrac{100}{250} = 0.40$

Thus, composition of the liquid mixture will be

Mole fraction of $A(\chi_A) = 0.40$

Mole fraction of $B(\chi_B) = 1 - 0.40 = 0.60$

$\therefore \quad p_A = \chi_A \times p_A^\circ$

$= 0.40 \times 450$ mm of Hg $= 180$ mm of Hg

$p_B = \chi_B \times p_B^\circ$

$= 0.60 \times 700$ mm of Hg $= 420$ mm of Hg

Thus, in vapour phase, mole fraction of

$$A = \frac{p_A}{p_A + p_B} = \frac{180}{180+420} = 0.30$$

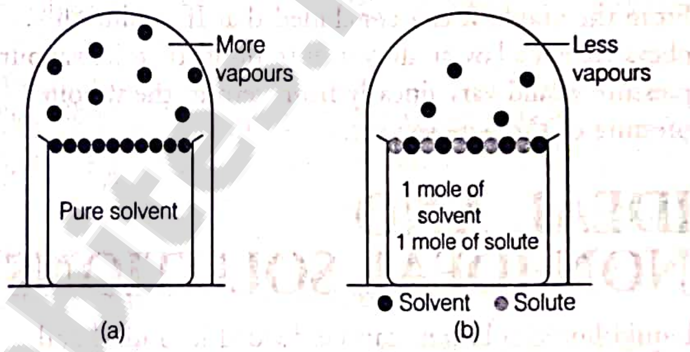
Mole fraction of $B = 1 - 0.30 = 0.70$

Vapour Pressure of Solutions of Solids in Liquids

When solids like sodium chloride, glucose, urea are dissolved in liquids, solutions of solids in liquids are obtained. Some physical properties of these solutions are quite different from those of pure solvents.

If a non-volatile solute is added to a solvent to form a solution, the vapour pressure of the solution depends only upon the solvent. This vapour pressure of the solution at the given temperature is found to be lower than the vapour pressure of the pure solvent at the same temperature. This decrease in vapour pressure occurs because in solid-liquid solution, the surface has both solute and solvent molecules; thereby the fraction of the surface covered by the solvent molecules gets reduced.

Consequently, the number of solvent molecules escaping from the surface is correspondingly reduced, thus, the vapour pressure is also reduced.



Decrease in the vapour pressure of the solvent on account of the presence of solute in the solvent. (a) evaporation of the molecules of the solvent (denoted by dark dots) from its surface. (b) in a solution, solute particles (denoted by light dots) also occupy part of the surface area.

The decrease in the vapour pressure of solvent depends on the amount of non-volatile solute present in the solution, irrespective of its nature.

e.g. If we add 1 mole of sucrose to 1 kg of water and 1 mole of urea to the same quantity of water in another container at the same temperature, the decrease in vapour pressure of water is nearly similar to that produced by adding 1.0 mole of urea to the same quantity of water at the same temperature.

Raoult's law in its general form can be stated as, for any solution, the **partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction.**

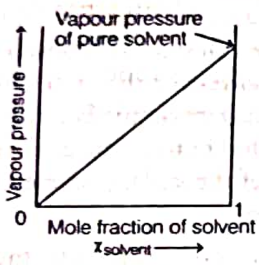
Raoult's Law for Liquid Solutions Containing Non-volatile Solutes (Solid in Liquid Solution)

In a binary solution (when the solute is non-volatile and non-electrolyte), only the solvent molecules are present in the vapour phase and contribute to vapour pressure. Let p_1 be the vapour pressure of the solvent, χ_1 be its mole fraction and p_1° be its vapour pressure in the pure state.

Then, according to Raoult's law,

$$p_1 \propto \chi_1 \text{ and } p_1 = \chi_1 p_1^\circ$$

The proportionality constant is equal to the vapour pressure of pure solvent, p_1°.



A plot between the vapour pressure and mole fraction of the solvent

From the graph, it can concluded that If a solution obeys Raoult's law at all concentrations, then its vapour pressure would vary linearly from zero to the vapour pressure of the pure solvent.

IDEAL AND NON-IDEAL SOLUTIONS

Liquid-liquid solutions can be divided into ideal and non-ideal solutions on the basis of Raoult's law.

Ideal Solutions

The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions.

The characteristic properties of these solutions are :

(i) The enthalpy of mixing the pure components to form the solution is zero, i.e. $\Delta_{mix} H = 0$.

(ii) The volume of mixing is also zero, i.e. $\Delta_{mix} V = 0$.

The above two properties mean that no heat is absorbed or evolved when the components are mixed. Also the volume of the solution is equal to the sum of volumes of the two components.

Explanation of Ideal Behaviour

At the molecular level, an ideal behaviour of solutions can be explained by considering the binary solution of components A and B in which the intermolecular interactions A—B are of the same magnitude as the intermolecular interactions found in the pure components, i.e. A—A interactions and B—B interactions. If such interactions occur the solution is said to be ideal. Practically, no solution is ideal but some solutions are nearly ideal in behaviour under certain conditions.

Examples of this type of solutions are :

(i) *n*-hexane + *n*-heptane

(ii) Bromoethane + chloroethane

(iii) Benzene + toluene

(iv) Chlorobenzene + bromobenzene

Non-Ideal Solutions

When a solution does not obey Raoult's law over the entire range of concentration, it is called non-ideal solution.

The characteristic properties of such solutions are :

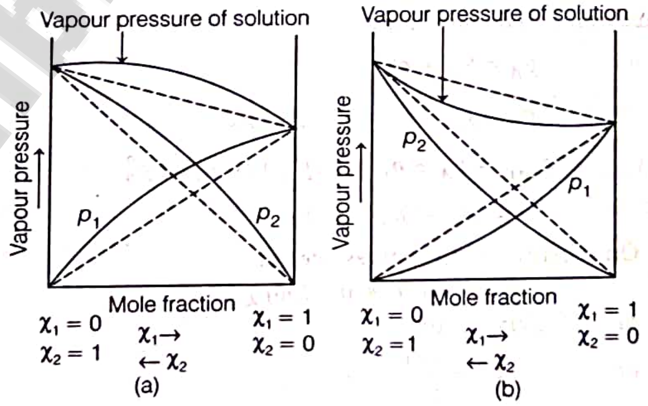
(i) The enthalpy of mixing of pure components to form the solution is not zero. It may have a positive or negative value. i.e. $\Delta_{mix} H \neq 0$

(ii) The volume of mixing is also not zero. Volume may increase or decrease after mixing. i.e. $\Delta_{mix} V \neq 0$.

The vapour pressures of these solutions are either higher or lower than that predicted by Raoult's law.

If it is higher, then the solution exhibits **positive deviation** and if it is lower, then it exhibits **negative deviation** from Raoult's law.

The plots of vapour pressure as a function of mole fractions for such solutions are shown in the figures given below :



The vapour pressures of two component systems as a function of composition (a) a solution that shows positive deviation from Raoult's law and (b) a solution that shows negative deviation from Raoult's law

Explanation of Non-ideal Behaviour

In case of positive deviation from Raoult's law, intermolecular interactions, i.e. A — B interactions are weaker than those between A — A or B — B, i.e. in this case, the intermolecular attractive forces between the solute and solvent molecules are weaker than those between solute-solute and solvent-solvent molecules.

This means that molecules of A (or B) will find it easier to escape than being in liquid state. This increases the vapour pressure and gives a positive deviation [Fig. (a)]. This deviation is shown by ethanol and acetone solution. In pure ethanol, molecules are hydrogen bonded.

On adding acetone, the hydrogen bonds break. Due to weakening of interactions, the solution shows positive deviation.

Other examples of this type of solutions are :

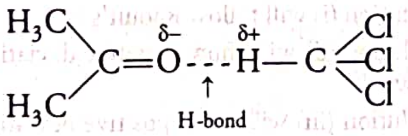
(i) Carbon disulphide + acetone

(ii) Ethanol + cyclohexane

(iii) Acetone + benzene

In case of **negative deviation** from Raoult's law; intermolecular interactions, i.e. $A—B$ interactions are stronger than those between $A—A$ or $B—B$.
This decreases the escaping tendency of molecules of A or B component and consequently, the vapour pressure decreases resulting in negative deviation from Raoult's law [Fig. (b)].

A mixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown below.



Other examples of this type of solutions are:

(i) Chloroform + diethyl ether

(ii) Phenol + aniline

(iii) Water + nitric acid

Difference between solutions having positive deviation from ideal behaviour and the solutions having negative deviation from ideal behaviour are given in the table below:

Solutions having positive deviation from ideal behaviour	Solutions having negative deviation from ideal behaviour
The intermolecular interactions, i.e. $A — B$ interactions are weaker than in pure components, i.e. between $A—A$ or $B—B$.	The intermolecular interactions, i.e. $A — B$ interactions are stronger than in pure components, i.e. between $A — A$ or $B — B$.
$p_1 > p_1^\circ\chi_1$ and $p_2 > p_2^\circ\chi_2$	$p_1 < p_1^\circ\chi_1$ and $p_2 < p_2^\circ\chi_2$
$\Delta_{mix}H$ = positive (endothermic)	$\Delta_{mix}H$ = negative (exothermic)
$\Delta_{mix}V$ = positive	$\Delta_{mix}V$ = negative
Heating increases solubility.	Heating decreases solubility.

Depending upon the extent of deviation from Raoult's law, a new category of binary mixtures, known as azeotropes, is formed. It is discussed below.

Azeotropes (Constant Boiling Mixtures)

The binary mixtures (liquid mixtures) having the same composition in liquid and vapour phase and that boil at constant temperature are called **azeotropic mixtures or azeotropes.**

In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called **minimum boiling azeotropes** and **maximum boiling azeotropes**. The azeotropes distil over as if they are pure liquids.

Minimum Boiling Azeotropes

The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotropes at specific compositions. For one of the intermediate composition, the total vapour pressure of such a solution will be the highest and boiling point will be the lowest.

e.g. Ethanol-water mixture on fractional distillation gives a solution containing approximately 95% by volume of ethanol. After achieving this composition, no further separation occurs as the liquid and vapour have the same composition.

Maximum Boiling Azeotropes

The solutions which show a large negative deviation from Raoult's law form maximum boiling azeotropes at specific compositions. As the total vapour pressure becomes less than the corresponding ideal solution of same composition. So, the boiling points of such solutions are increased. e.g. Azeotrope formed from nitric acid and water has the approximate composition of 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

Difference between ideal and non-ideal solutions

Ideal solution	Non-ideal solution
The components obey Raoult's law at all temperature and concentrations. i.e. $p_A = p_A^\circ\chi_A$ and $p_B = p_B^\circ\chi_B$	The components do not obey Raoult's law. They show positive and negative deviations from Raoult's law, i.e. $p_A \neq p_A^\circ\chi_A$ and $p_B \neq p_A^\circ\chi_B$
On mixing, there is no enthalpy change. $\Delta_{mix}H = 0$	On mixing, there is an enthalpy change. $\Delta_{mix}H \neq 0$
On mixing, there is also no change in volume. $\Delta_{mix}V = 0$	On mixing, there is a change in volume as well. $\Delta_{mix}V \neq 0$
Interactions between components are similar to those in pure components.	Interactions between components are different from those of pure components.

TOPIC PRACTICE 3

OBJECTIVE Type Questions

1. When 1 mole of benzene is mixed with 1 mole of toluene. The vapour will contain (Given : vapour of benzene = 12.8 kPa and vapour pressure of toluene = 3.85 kPa). **CBSE SQP 2021**
   (a) equal amount of benzene and toluene as it forms an ideal solution
   (b) unequal amount of benzene and toluene as it forms a non-ideal solution
   (c) higher percentage of benzene
   (d) higher percentage of toluene

2. p_A and p_B are the vapour pressure of pure liquid components A and B respectively of an ideal binary solution. If x_A represents the mole fraction of component A, the total pressure of the solution will be
   (a) $p_A + x_A (p_B - p_A)$ (b) $p_A + x_A (p_A - p_B)$
   (c) $p_B + x_A (p_B - p_A)$ (d) $p_B + x_A (p_A - p_B)$

3. Vapour pressure of pure A is 70 mm of Hg at 25°C. It forms an ideal solution with 'B' in which mole fraction of A is 0.8. If the vapour pressure of the solution is 84 mm of Hg at 25°C, the vapour pressure of pure B at 25°C is
   (a) 56 mm (b) 70 mm
   (c) 140 mm (d) 28 mm

4. At 40°C, the vapour pressure of pure liquids, benzene and toluene, are 160 mmHg and 60 mmHg respectively. At the same temperature, the vapour pressure of an equimolar solution of the two liquids, assuming the ideal solution should be
   (a) 140 mmHg
   (b) 110 mmHg
   (c) 220 mmHg
   (d) 100 mmHg

5. Which one of the following pairs will not form an ideal solution? **CBSE 2021 (Term I)**
   (a) Benzene and toluene
   (b) n-hexane and n-heptane
   (c) Ethanol and acetone
   (d) Bromoethane and chloroethane

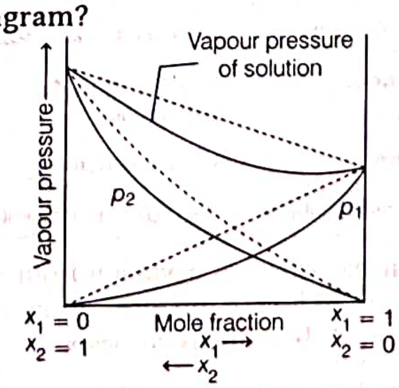
6. Solution of bromoethane and chloroethane
   (a) obeys Raoult's law over the entire range of concentration
   (b) is a non-ideal solution
   (c) has $\Delta_{mix} V \neq 0$
   (d) All of the above

7. On the basis of information given below mark the correct option.
   Information
   (i) In bromoethane and chloroethane mixture intermolecular interactions of A–A and B–B type are nearly same as A–B type interactions.
   (ii) In ethanol and acetone mixture A–A or B–B type intermolecular interactions are stronger than A–B type interactions.
   (iii) In chloroform and acetone mixture A–A or B–B type intermolecular interactions are weaker than A–B type interactions.
   (a) Solution (ii) and (iii) will follow Raoult's law
   (b) Solution (i) will follow Raoult's law
   (c) Solution (ii) will show negative deviation from Raoult's law
   (d) Solution (iii) will show positive deviation from Raoult's law

8. Which of the following azeotropic solutions has the boiling point less than the boiling point of its constituents molecules? **All India 2020**
   (a) $CHCl_3$ and CH_3COCH_3
   (b) CS_2 and CH_3COCH_3
   (c) CH_3CH_2OH and CH_3COCH_3
   (d) CH_3CHO and CS_2

9. An azeotropic solution of two liquids has a boiling point higher than either of the two when it **CBSE 2021 (Term I)**
   (a) shows a negative deviation from Raoult's law
   (b) shows a positive deviation from Raoult's law
   (c) is saturated
   (d) shows no deviation from Raoult's law

10. Which of the following statements is/are true for the diagram?



   (a) The escaping tendency of molecule decreases for each component
   (b) Vapour pressure of the solution decreases
   (c) Solution shows negative deviation from Raoult's law
   (d) All of the above

VERY SHORT ANSWER Type Questions

11. What role does the molecular interaction play in solution of alcohol and water? **NCERT**

12. How is the vapour pressure of a solvent affected when a non-volatile solute is dissolved in it? **Delhi 2014 C**

13. Define Raoult's law in its general form in reference to solutions. **Delhi 2011; All India 2011; Foreign 2011**

Or State 'Raoult's law' for a solution of volatile liquids. **Delhi 2020, 2010 C; Foreign 2009 C**

14. If the vapour pressure of C_2H_5OH at 298 K is 40 mm of Hg. Its mole fraction in a solution with CH_3OH is 0.8. What will be its vapour pressure in solution, if it obeys Raoult's law?

15. When water and nitric acid are mixed together, a rise in temperature is observed. What type of azeotropic mixture is obtained?

SHORT ANSWER Type I Questions

16. Why is the vapour pressure of a solution of glucose in water lower than that of water? **NCERT Exemplar**

Or If a table spoon of sugar is added to water, then what happens to vapour pressure of water?

17. What is the similarity between Raoult's and Henry's laws? **Delhi 2020, All India 2014**

18. Define the following
    (i) Ideal solution **All India 2014, 2013, 2012; Delhi 2010 C**
    (ii) Molarity (M) **Delhi 2017**

19. (i) Gas (A) is more soluble in water than gas (B) at the same temperature. Which one of the two gases will have the higher value of K_H (Henry's constant) and why?
    (ii) In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes? **All India 2016**

20. What type of deviation is shown by a mixture of ethanol and acetone? Give reason. **Delhi 2014**

21. On mixing liquid X and liquid Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution? What change in temperature would you observe after mixing liquids X and Y? **All India 2015**

22. Define azeotropes. What type of azeotrope is formed by the positive deviation from Raoult's law? Give an example. **All India 2014, 2013; Delhi 2015**

23. What type of azeotropic mixture will be formed by a solution of acetone and chloroform? Justify on the basis of strength of intermolecular interactions that develop in the solution. **All India 2019**

SHORT ANSWER Type II Questions

24. 100 g of liquid A (molar mass 140 g mol^{-1}) was dissolved in 1000 g of liquid B (molar mass 180 g mol^{-1}). The vapour pressure of pure liquid B was found to be 500 torr.
    Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution, if the total vapour pressure of the solution is 475 torr. **NCERT**

25. Benzene and toluene form ideal solution over the entire range of composition. The vapour pressures of pure benzene and toluene at 300 K are 50.71 mm of Hg and 32.06 mm of Hg, respectively. Calculate the mole fraction of benzene in the vapour phase, if 80 g of benzene is mixed with 100 g of toluene. **NCERT**

26. At 25°C the vapour pressures of benzene (C_6H_6) and toluene (C_7H_8) are 93.4 torr and 26.9 torr, respectively. A solution is made by mixing 35.0 g of benzene and 65.0 g of toluene. At what applied pressure, in torr, will this solution boil at 25°C ?

27. At some temperature, the vapour pressure of pure C_6H_6 is 0.256 bar and that of pure $C_6H_5CH_3$ (toluene) is 0.0925 bar. If the mole fraction of toluene in solution is 0.6. Then,
    (i) what will be the total pressure of the solution?
    (ii) what will be the mole fraction of each component in vapour phase?

LONG ANSWER Type Questions

28. What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{mix}H$ related to positive and negative deviations from Raoult's law? **NCERT**

29. (i) Two liquids A and B boil at 155°C and 190°C, respectively. Which of them has a higher vapour pressure at 80°C?

(ii) Heptane and octane form ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa, respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35.0 g of octane? **NCERT**

(iii) The vapour pressure of water is 12.3 kPa at 300 K. Calculate the vapour pressure of one molal solution of non-volatile, non-ionic solute in water. **NCERT**

30. Vapour pressure of pure acetone and chloroform at 328 K are 741.8 mm of Hg and 632.8 mm of Hg, respectively. Assuming that they form ideal solution over the entire range of composition, plot p_{total}, $p_{chloroform}$ and $p_{acetone}$ as a function of $\chi_{acetone}$. The experimental data observed for different compositions of mixture is

$100 \times \chi_{acetone}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
$p_{acetone}$/mm of Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{chloroform}$/mm of Hg	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7

Plot this data also on the same graph paper. Indicate whether it has positive deviation or negative deviation from the ideal solution. **NCERT**

HINTS AND EXPLANATIONS

1. (c) When 1 mole of benzene is mixed with 1 mole of toluene. The vapours will contain higher percentage of benzene. Vapour pressure of benzene is greater than vapour pressure of toluene. So, the vapours above the solution majorly consist of benzene vapours.

2. (d) Total pressure, $p_T = p'_A + p'_B$ ...(i)

We know that $p'_A = p_A x_A$ and $p'_B = p_B x_B$

Substituting the values of p'_A and p'_B in Eq. (i)

$$p_T = p_A x_A + p_B x_B \quad ...(ii)$$

$$[x_A + x_B = 1 \Rightarrow x_A = 1 - x_B \text{ or } x_B = 1 - x_A]$$

From Eq. (ii)

$$p_T = p_A x_A + p_B(1 - x_A) = p_A x_A + p_B - p_B x_A$$

$$p_T = p_B + x_A(p_A - p_B)$$

3. (c) Given, $p^\circ_A = 70$ mm Hg

$$x_A = 0.8$$

$$\therefore \quad x_B = (1 - 0.8) = 0.2 \text{ and } p = 84 \text{ mmHg}$$

According to Raoult's law,

$$p = p^\circ_A\, x_A + p^\circ_B\, x_B$$

$$84 = 0.8 \times 70 + 0.2 \times p^\circ_B$$

$$p^\circ_B = \frac{28}{0.2} = 140 \text{ mm Hg}$$

4. (b) For ideal solution, $p_{total} = p_1{}^\circ x_1 + p_2{}^\circ x_2$

$$= 160 \times \frac{1}{2} + 60 \times \frac{1}{2}$$

$$= 110 \text{ mmHg}$$

5. (c) Ethanol and acetone solution will not form an ideal solution and shows positive deviation from Raoult's law.

6. (a) Bromoethane and chloroethane form ideal solution and thus obeys Raoult's law over the entire range of concentration.

7. (b) For an ideal solution, the A—A or B—B type intermolecular interaction is nearby equal to A—B type interaction. Here, a mixture of bromoethane and chloroethane is an example of ideal solution.

On the other hand chloroform and acetone mixture is an example of non-ideal solution having negative deviation from Raoult's law. So, (A—A) or (B—B) interaction must be stronger than A—B interaction. While ethanol-acetone mixture shows positive deviation from Raoult's due to weaker A—B interaction in comparison to A—A or A—B interaction.

8. (c) When the new interaction is weaker than those in the pure constituents, the boiling point of the resultant solution is less than that of the constituents. Such condition is found in case of non-ideal solution showing positive deviation from Raoult's law. Among the given solutions, mixture of CH_3CH_2OH and CH_3COCH_3 is non-ideal and show positive deviation. Hence, it has lesser boiling point or higher vapour pressure, than its constituents.

9. (a) Because of strong interactions between two liquids, the azeotropic solution is higher than either of the two. Hence, it shows a negative deviation from Raoult's law.

10. (d) Figure suggests that escaping tendency of molecules for each component decreases and consequently the vapour pressure decreases resulting in the negative deviation from Raoult's law.

11. There is strong hydrogen bonding in alcohol molecules as well as water molecules. On mixing these solutions, the molecular interactions are weakened. Hence, they show positive deviations from ideal behaviour. Therefore, the solution will have higher vapour pressure and lower boiling point than that of water and alcohol.

12. When a non-volatile solute is added to a solvent, its vapour pressure decreases because some of the surface

sites are occupied by solute molecules. Thus, less space is available for the solvent molecule to vaporise.

13. Raoult's law states that at a given temperature, for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

14. $p_{C_2H_5OH}$ = 32 mm of Hg Refer to example 1 on page 17.

15. When water and nitric acid are mixed together, a rise in temperature is observed. It shows a negative deviation from Raoult's law. Therefore, there occur a minimum in vapour pressure *versus* mole fraction graph and maximum in boiling point *versus* mole fraction graph of the solution. Hence, solution of nitric acid and water forms a maximum boiling azeotrope.

16. In the solution, the surface has both solute and solvent molecules, so the fraction of the surface covered by solvent molecules gets reduced. Thus, the number of solvent molecules escaping from the surface is reduced, resulting in lowering the vapour pressure.
So, the vapour pressure of the solution of glucose in water is lower than that of pure water.

17. Similarity between Raoult's and Henry's laws both the laws are applied to volatile component in solution. Both the laws state that the vapour pressure of one component is proportional to the mole fraction of that component.

18. (i) The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions. Refer to text on page 18.

(ii) Molarity is defined as the number of moles of solute dissolved in one litre or one cubic decimetre of the solution.

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

e.g. 0.25 mol L^{-1} (or 0.25 M) solution of NaOH means that 0.25 mole of NaOH has been dissolved in one litre (or one cubic decimetre).

19. Solubility is inversely proportional to K_H, i.e. Henry's constant of the gas.

(i) Greater the value of K_H, lower is the solubility of the gas. As gas (A) is more soluble in water than gas (B) at the same temperature, hence the gas (A) has lower value of K_H. In other words, gas (B) has higher value of K_H than gas (A) at the same temperature.

(ii) In non-ideal solutions, the solutions that show large negative deviation from Raoult's law form maximum boiling azeotropes. e.g. Mixture of nitric acid and water.

20. A mixture of ethanol and acetone shows positive deviation because in this case, $A—B$ interactions are weaker than $A—A$ and $B—B$ interactions. Due to this, vapour pressure increases which results in positive deviation.

21. **Hint** It is an example of negative deviation. Since, $\Delta_{mix} V$ is negative hence $\Delta_{mix} H$ is also negative and temperature rises. Refer to text on page 18.

22. Refer to text on pages 19.

23. The mixture of acetone and chloroform is an example of maximum boiling azeotrope. It shows negative deviation from Raoult's law because of increase in intermolecular forces of attraction between acetone and chloroform, since they form hydrogen bonds between them.

24. Number of moles of liquid A (solute)

$$= \frac{100 \text{ g}}{140 \text{ g mol}^{-1}} = \frac{5}{7} \text{ mol}$$

$$\text{Number of moles of liquid } B = \frac{1000 \text{ g}}{180 \text{ g mol}^{-1}} = \frac{50}{9} \text{ mol}$$

$\therefore$ Mole fraction of A in the solution (χ_A)

$$= \frac{5/7}{5/7 + 50/9} = \frac{5/7}{395/63} = \frac{5}{7} \times \frac{63}{395} = \frac{45}{395} = 0.114$$

$\therefore$ Mole fraction of B in the solution (χ_B)

$$= 1 - 0.114 = 0.886$$

Also, given $\quad p_B^\circ = 500$ torr

According to Raoult's law,

$$p_A = \chi_A p_A^\circ = 0.114 \times p_A^\circ \quad \text{...(i)}$$

$$p_B = \chi_B p_B^\circ = 0.886 \times 500 = 443 \text{ torr}$$

$$p_{\text{total}} = p_A + p_B$$

or $\quad 475 = 0.114 p_A^\circ + 443$

or $\quad p_A^\circ = \dfrac{475 - 443}{0.114} = 280.7$ torr

Substituting the value of p_A° in Eq. (i), we get

$$p_A = 0.114 \times 280.7 \text{ torr} = 32 \text{ torr}$$

25. Molar mass of benzene $(C_6H_6) = 78 \text{ g mol}^{-1}$

Molar mass of toluene $(C_7H_8) = 92 \text{ g mol}^{-1}$

$n_{C_6H_6}$ (number of moles of benzene)

$$= \frac{80 \text{ g}}{78 \text{ g mol}^{-1}} = 1.026 \text{ mol}$$

$n_{C_7H_8}$ (number of moles of toluene)

$$= \frac{100 \text{ g}}{92 \text{ g mol}^{-1}} = 1.087 \text{ mol}$$

Mole fraction of benzene,

$$\chi_{C_6H_6} = \frac{1.026 \text{ mol}}{(1.026 + 1.087) \text{ mol}} = 0.486$$

Mole fraction of toluene

$$\chi_{C_7H_8} = 1 - 0.486 = 0.514$$

Applying Raoult's law,
Partial vapour pressure of benzene in solution

$$p_{C_6H_6} = p^\circ_{C_6H_6} \times \chi_{C_6H_6}$$
$$= (50.71 \text{ mm of Hg}) \times (0.486)$$
$$= 24.65 \text{ mm of Hg}$$

Partial vapour pressure of toluene in solution

$$p_{C_7H_8} = p^\circ_{C_7H_8} \times \chi_{C_7H_8} = 32.06 \text{ mm of Hg} \times 0.514$$
$$= 16.48 \text{ mm of Hg}$$

Total vapour pressure of solution

$$p = 24.65 \text{ mm of Hg} + 16.48 \text{ mm of Hg}$$
$$= 41.13 \text{ mm of Hg}$$

Mole fraction of benzene in vapour phase

$$= \frac{\chi_{C_6H_6} \times p^\circ_{C_6H_6}}{p_{total}} = \frac{0.486 \times 50.71}{41.13} = 0.6$$

26. This solution of benzene and toluene will boil at 25°C when the pressure above the solution is equal to the sum of the vapour pressures of benzene and toluene in the solution.

Partial vapour pressure of benzene, $p^\circ_{C_6H_6} = 93.4$ torr

Partial vapour pressure of toluene,

$$p^\circ_{C_6H_5CH_3} = 26.9 \text{ torr}$$

Mass of C_6H_6 = 35 g and mass of $C_6H_5CH_3$ = 65 g

Molar mass of $C_6H_6 = 12 \times 6 + 1 \times 6$
$= 72 + 6 = 78 \text{ g mol}^{-1}$

Therefore, the number of moles of C_6H_6,

$$n_{C_6H_6} = \frac{35}{78} = 0.449$$

Molar mass of $C_6H_5CH_3 = 12 \times 6 + 1 \times 5 + 12 + 1 \times 3$
$= 92 \text{ g mol}^{-1}$

Therefore, the number of moles of $C_6H_5CH_3$,

$$n_{C_6H_5CH_3} = \frac{65}{92} = 0.707$$

Now, the mole fractions of C_6H_6 and $C_6H_5CH_3$ are

$$\chi_{C_6H_6} = \frac{n_{C_6H_6}}{n_{C_6H_6} + n_{C_6H_5CH_3}}$$
$$= \frac{0.449}{0.449 + 0.707} = \frac{0.449}{1.156} = 0.388$$
$$\chi_{C_6H_5CH_3} = \frac{n_{C_6H_5CH_3}}{n_{C_6H_5CH_3} + n_{C_6H_6}} = \frac{0.707}{0.707 + 0.449}$$
$$= \frac{0.707}{1.156} = 0.612$$

Therefore, vapour pressure of C_6H_6 and $C_6H_5CH_3$ are

$$p_{C_6H_6} = p^\circ_{C_6H_6} \times \chi_{C_6H_6}$$
$$= 93.4 \times 0.388 = 36.24 \text{ torr}$$
$$p_{C_6H_5CH_3} = p^\circ_{C_6H_5CH_3} \times \chi_{C_6H_5CH_3}$$
$$= 26.9 \times 0.612 = 16.46 \text{ torr}$$

Total vapour pressure of the solution,

$$p_{total} = p_{C_6H_6} + p_{C_6H_5CH_3}$$
$$= 36.24 + 16.46 = 52.7 \text{ torr}$$

27. (i) According to Raoult's law,

For toluene, $p_1 = p^\circ_1 \times \chi_1$

$p^\circ_1 = 0.0925$ bar

and $\chi_1 = 0.6$

Then, $p_1 = 0.0925 \times 0.6 = 0.0555$ bar

For benzene, $p_2 = p^\circ_2 \times \chi_2$

Mole fraction of benzene,

$$\chi_2 = 1 - \chi_1 = 1 - 0.6 = 0.4$$

and $p^\circ_2 = 0.256$ bar

Then, $p_2 = 0.256 \times 0.4 = 0.1024$ bar

Total vapour pressure of solution

$$p_{total} = p_1 + p_2$$
$$= 0.0555 + 0.1024 = 0.158 \text{ bar}$$

(ii) Mole fraction of toluene in vapour phase

$$y_1 = \frac{p_1}{p_{total}} = \frac{0.0555}{0.158} = 0.351$$

Mole fraction of benzene in vapour phase

$$y_2 = \frac{p_2}{p_{total}} = \frac{0.1024}{0.158} = 0.648$$

28. Refer to text on pages 18 and 19.

29. (i) *A* is more volatile, therefore has higher vapour pressure.

(ii) Given that, $p^\circ_{heptane} = 105.2$ kPa,

$$p^\circ_{octane} = 46.8 \text{ kPa}$$

Molar mass of heptane $(C_7H_{16}) = 100 \text{ g mol}^{-1}$

(As $C_7H_{16} = 7 \times 12 + 16 = 84 + 16 = 100$)

Molar mass of octane $(C_8H_{18}) = 114 \text{ g mol}^{-1}$

(As $C_8H_{18} = 8 \times 12 + 18 = 96 + 18 = 114$)

Number of moles of 26.0 g heptane

$$= \frac{26.0 \text{ g}}{100 \text{ g mol}^{-1}} = 0.26 \text{ mol}$$

Number of moles of 35.0 g octane

$$= \frac{35.0 \text{ g}}{114 \text{ g mol}^{-1}} = 0.31 \text{ mol}$$

$$\chi_{heptane} = \frac{0.26 \text{ g}}{0.26 + 0.31} = 0.456$$
$$\chi_{octane} = 1 - 0.456 = 0.544$$
$$p_{heptane} = 0.456 \times 105.2 \text{ kPa} = 47.97 \text{ kPa}$$
$$p_{octane} = 0.544 \times 46.8 \text{ kPa} = 25.46 \text{ kPa}$$
$$p_{total} = 47.97 + 25.46 = 73.43 \text{ kPa}$$

(iii) As solution is 1 molal, it means that 1 mole of solute is dissolved in 1000 g of solvent (water).

No. of moles of solute = 1 mol, $p^\circ_{solvent} = 12.3$ kPa

No. of moles of water $= \frac{1000}{18} = 55.55$ mol

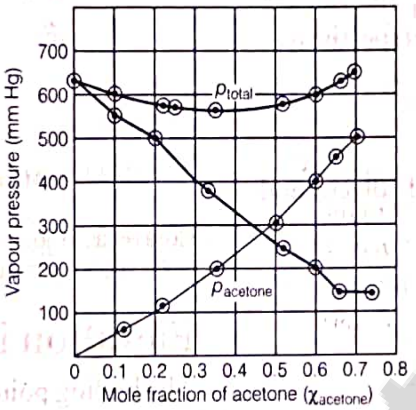
Total moles = 56.55 mol

Mole fraction of water $= \frac{\chi_1(\text{solvent})}{\chi_1 + \chi_2(\text{solution})} = \frac{55.55}{56.55}$

$$p_{solution} = p^\circ_{solvent} \times \chi_{H_2O}$$
$$p_{solution} = 12.3 \times \frac{55.55}{56.55} = 12.08 \text{ kPa}$$

30.

$\chi_{acetone}$	0.0	0.118	0.234	0.360	0.508	0.582	0.645	0.721
$p_{acetone}$/mm of Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{chloroform}$/mm of Hg	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7
p_{total}	632.8	603.1	579.7	562.4	580.9	600.0	615.9	642.5



As the plot for p_{total} dips downwards, hence the solution shows negative deviation from Raoult's law.

|TOPIC 4|
Colligative Properties and Determination of Molar Mass

COLLIGATIVE PROPERTIES

The word colligative is originated from Latin in which 'co' means together and 'ligate' means to bind.

The properties of solutions which depend only on the number of solute particles irrespective of their nature, relative to the total number of particles present in the solution, are called colligative properties.

There are four important colligative properties :

(i) Relative lowering of vapour pressure
(ii) Elevation in boiling point
(iii) Depression in freezing point
(iv) Osmosis and osmotic pressure

Relative Lowering of Vapour Pressure

We have studied that, on adding non-volatile solute to a solvent, the vapour pressure of the solution decreases. Lowering of vapour pressure depends only on the concentration of the solute particles and it is independent of their identity.

Let χ_1 is the mole fraction of solvent, χ_2 is that of solute, p_1° is the vapour pressure of pure solvent and p is that of solution.Since, solute is non-volatile, so the vapour pressure of the solution (p_1) will be only due to the solvent. Thus, according to **Raoult's law**,

$$p_1 = p_1^\circ \chi_1 \quad \text{or} \quad p = p_1 = p_1^\circ \chi_1$$

This, equation establishes a relation between vapour pressure of the solution, mole fraction and vapour pressure of the solvent.

Since, χ_1 is always less than 1, hence vapour pressure of the solution p will always be less than the vapour pressure of pure solvent (p_1°).

So, lowering in vapour pressure of solvent is given as

$$\Delta p_1 = p_1^\circ - p_1 = p_1^\circ - p_1^\circ \chi_1 = p_1^\circ(1-\chi_1)$$

But $\quad \chi_1 = 1-\chi_2 \quad \text{or} \quad \chi_2 = 1-\chi_1$

So, $\quad \Delta p_1 = p_1^\circ \chi_2 \quad \text{or} \quad \chi_2 = \dfrac{\Delta p_1}{p_1^\circ} = \dfrac{p_1^\circ - p_1}{p_1^\circ}$

So, relative lowering in vapour pressure of an ideal solution containing the non-volatile solute is equal to the mole fraction of the solute at a given temperature.

In a solution containing several non-volatile solutes, the lowering of the vapour pressure depends on the sum of the mole fraction of different solutes.

Determination of Molar Mass of Solute

To express the lowering of vapour pressure in terms of molar mass, let W_1, W_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute, respectively.

As, we know that $$\chi_2 = \frac{n_2}{n_1 + n_2}$$

where, n_1 and n_2 are the number of moles of solvent and solute, respectively.

Since, $$\chi_2 = \frac{W_2 / M_2}{\frac{W_1}{M_1} + \frac{W_2}{M_2}}$$

But for dilute solutions, $\frac{W_2}{M_2} << \frac{W_1}{M_1}$

or $n_2 << n_1$

So, $$\frac{W_1}{M_1} + \frac{W_2}{M_2} \approx \frac{W_1}{M_1} \quad \text{or} \quad \chi_2 = \frac{W_2/M_2}{W_1/M_1}$$

So, $$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{W_2 M_1}{W_1 M_2} \quad \text{or} \quad \frac{p_1^\circ - p_1}{p_1^\circ} = \frac{n_2}{n_1}$$

So, molar mass of solute can be determined by

$$\boxed{M_2 = \frac{W_2 M_1}{W_1 \left(\frac{p_1^\circ - p_1}{p_1^\circ} \right)}}$$

EXAMPLE |1| An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute? **NCERT**

Addition of non-volatile solute in a solution results in relative lowering of vapour pressure. For dilute solution, molar mass of solute can be determined by using the formula,

$$M_2 = \frac{W_2 M_1}{W_1 \left(\frac{p_1^\circ - p_1}{p_1^\circ} \right)}$$

Sol. Vapour pressure of pure water at the boiling point

$$(p_1^\circ) = 1 \text{ atm} = 1.013 \text{ bar}$$

Vapour pressure of solution $(p) = 1.004$ bar (Given)

2% non-volatile solute means

Mass of solute $(W_2) = 2$ g

Mass of solution $= 100$ g

$\therefore$ Mass of solvent $(W_1) = 98$ g

Applying Raoult's law for dilute solution, as n_2 (moles of solute) is very small in comparison to n_1 (moles of solvent).

$\therefore$ n_2 can be neglected from denominator.

Lowering in vapour pressure,

$$\frac{p_1^\circ - p}{p_1^\circ} = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} = \frac{W_2 / M_2}{W_1 / M_1} = \frac{W_2}{M_2} \times \frac{M_1}{W_1}$$

$$\frac{(1.013 - 1.004)}{1.013 \text{ bar}} = \frac{2 \text{ g}}{M_2} \times \frac{18 \text{ g mol}^{-1}}{98 \text{ g}}$$

or $$M_2 = \frac{2 \times 18}{98} \times \frac{1.013}{0.009} \text{ g mol}^{-1} = 41.35 \text{ g mol}^{-1}$$

Note Relative lowering in vapour pressure is a colligative property while vapour pressure and lowering in vapour pressure are not.

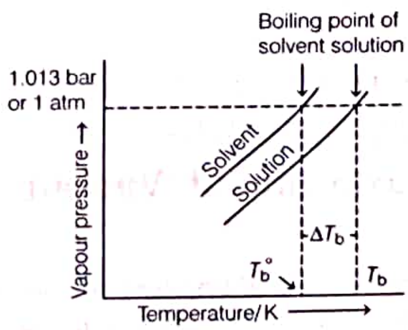
Elevation in Boiling Point

The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure. Generally, the vapour pressure of liquid increases with increase of temperature but vapour pressure of the solvent decreases in the presence of non-volatile solute.

e.g. The vapour pressure of an aqueous solution of sucrose is less than 1.013 bar at 373.15 K (100°C). In order to make this solution boil, its vapour pressure must be increased to 1.013 bar by raising the temperature above the boiling temperature of pure solvent (water).

So, we can say that when a non-volatile solute is added to a solvent, the boiling point of the solution is always higher than that of pure solvent, e.g. a solution of 1 mole of sucrose in 1000 g of water boils at 373.52 K at 1 atm pressure.

This difference in the boiling points of the solution (T_b) and pure solvent (T_b°) is called as **elevation in boiling point** (ΔT_b). Elevation in boiling point depends on the number of solute molecules rather than their nature.



The vapour pressure curve for solution lies below the curve for pure water. The figure shows that ΔT_b denotes the elevation in boiling point of a solvent in solution

The given figure depicts the variation of vapour pressure of the pure solvent and solution as a function of temperature.

Elevation in boiling point is given by

$$\Delta T_b = T_b - T_b^\circ$$

Experiments have shown that for dilute solution, the elevation in boiling point is directly proportional to the molal concentration of the solute in a solution (m).

Thus, $\Delta T_b \propto m$

or $\Delta T_b = K_b m$

where, m (molality) is the number of moles of solute dissolved in 1 kg of solvent and K_b is the constant of proportionality, called **molal boiling point elevation constant** or **ebullioscopic constant**. The unit of K_b is K kg mol^{-1}.

If $m = 1$ molal

Then, $\Delta T_b = K_b$

Thus, molal boiling point elevation constant, K_b is defined as the elevation in boiling point for 1 molal solution, i.e. a solution containing 1 g mole of solute dissolved in 1000 g of the solvent.

Determination of Molar Mass of Solute

If W_2 gram of solute of molar mass M_2 is dissolved in W_1 gram of solvent, then molality, m of the solution is given as:

$$\text{Molality }(m) = \frac{\text{Moles of solute }(n_2) \times 1000}{\text{Weight of solvent }(W_1)\text{ (in gram)}}$$

where, n_2 is the number of moles of solute.

$$\text{Moles of solute }(n_2) = \frac{W_2}{M_2}$$

Thus, $$m = \frac{W_2 \times 1000}{M_2 \times W_1}$$

But $\Delta T_b = K_b m$

So, we get $$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1}$$

Therefore, $$M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$$

This expression is used to determine the molar mass of solute.

EXAMPLE |2| Boiling point of water at 750 mm of Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C?
[K_b for water is 0.52 K kg mol^{-1}] **NCERT Intext**

(i) Since, boiling point is changing, apply the formula for elevation in boiling point, $\Delta T_b = K_b \cdot m$

(ii) $m = \dfrac{W_B}{M_B \cdot W_A}$

So, $\Delta T_b = \dfrac{K_b \cdot W_B}{M_B \times W_A}$ or $W_B = \dfrac{\Delta T_b \times M_B \times W_A}{K_b}$

(iii) Find ΔT_b as $\Delta T_b = T_b = T_b - T_b^\circ$

T_b = Boiling point of solution

T_b° = Boiling point of pure solvent

Sol. Mass of water (W_A) = 500 g = 0.5 kg

Elevation in boiling point

$(\Delta T_b) = 100°\text{C} - 99.63°\text{C} = 0.37°\text{C} = 0.37\text{ K}$

Molal elevation constant (K_b) = 0.52 K kg mol^{-1}

Molar mass of sucrose ($C_{12}H_{22}O_{11}$)

$(M_B) = (12 \times 12) + (22 \times 1) + (16 \times 11) = 342\text{ g mol}^{-1}$

$$W_B = \frac{M_B \times \Delta T_b \times W_A}{K_b}$$

$$= \frac{(342\text{ g mol}^{-1}) \times (0.37\text{ K}) \times (0.5\text{ kg})}{(0.52\text{ K kg mol}^{-1})} = 121.7\text{ g}$$

Depression in Freezing Point

The freezing point is that temperature at which the solid and the liquid states of the substance have the same vapour pressure.

When a non-volatile solute is added to a solvent, the freezing point of thus formed solution is always lower than that of pure solvent as the vapour pressure of the solvent decreases in the presence of non-volatile solute. This difference in the freezing point is known as depression in freezing point.

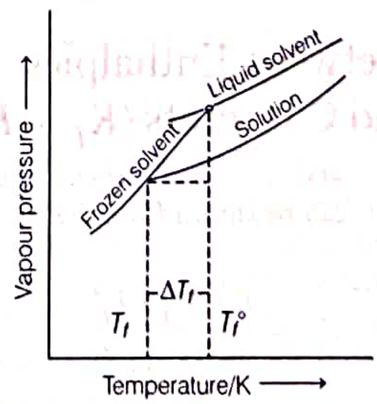


Figure showing ΔT_f, depression in freezing point of a solvent in a solution

If T_f° is the freezing point temperature (in kelvin) of pure solvent and T_f is the freezing point temperature (in kelvin) of the solution when non-volatile solute is dissolved in it then, depression in freezing point (ΔT_f) is given by $\Delta T_f = T_f^\circ - T_f$

For dilute solutions, $\Delta T_f \propto m$

or $$\boxed{\Delta T_f = K_f m}$$

where, m is the molal concentration (or molality) of the solution and the proportionality constant K_f, which depends on the nature of the solvent is known as **molal freezing point depression constant or molal depression constant or cryoscopic constant.**

The unit of K_f is K kg mol^{-1}.

If $m = 1$ molal, then $\Delta T_f = K_f$

Thus, molal freezing point depression constant is defined as the depression in freezing point for 1 molal solution, i.e. a solution containing 1g mole of solute dissolved in 1000 g of solvent.

Note

Elevation in boiling point and depression in freezing point are colligative properties while boiling and freezing points are not.

Determination of Molar Mass of Solute

Similar to elevation in boiling point,

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{W_1 \times M_2}$$

or $$\boxed{M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1}}$$

This expression is used to determine the molar mass of solute.

Relation between Enthalpies Change and Constants (K_f or K_b)

The values of K_f and K_b, which depend upon the nature of solvent, can be shown from the following relations:

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus} H}$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap} H}$$

where, R and M_1 stand for the gas constant and molar mass of the solvent, respectively and T_f and T_b denote the freezing point and the boiling point of the pure solvent respectively (in kelvin). $\Delta_{fus} H$ and $\Delta_{vap} H$ represent the enthalpies for the fusion and vaporisation of the solvent, respectively.

EXAMPLE |3| A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. Calculate the freezing point of a 5% glucose in water, if freezing point of pure water is 273.15 K. **NCERT**

Freezing point of pure water is 273.15 K (0°C) and that of given solution is 271 K, i.e. we have depression in freezing point. So,

(i) Apply the formula of depression in freezing point for cane sugar.

(ii) Similarly, find the depression in freezing point for glucose.

(iii) Compare the two equations to find the freezing point of glucose.

Sol. **For cane sugar solution**

Molality of sugar solution $= \frac{W_2}{M_2} \times \frac{1000}{W_1}$

Here, $W_2 = 5$ g, $M_2 = 342$ g mol^{-1} (sugar), $W_1 = 95$ g

$$\text{Molality} \quad (m) = \frac{5}{342} \times \frac{1000}{95} = 0.154$$

ΔT_f for sugar solution = 273.15 − 271 = 2.15 K

$$\Delta T_f = K_f \times m$$

$$\therefore \quad K_f = \frac{2.15}{0.154}$$

For glucose solution

Here, $W_2 = 5$ g, $m_2 = 180$ g mol^{-1} (glucose), $W_1 = 95$ g

Molality of glucose solution $= \frac{5}{180} \times \frac{1000}{95} = 0.2924$

$$\Delta T_f = K_f m$$

$$\therefore \quad \Delta T_f \text{ (glucose)} = \frac{2.15}{0.154} \times 0.2924 = 4.08$$

$\therefore$ Freezing point of glucose solution = 273.15 − 4.08 = 269.07 K

Osmosis and Osmotic Pressure

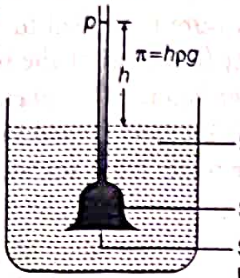
Osmosis

The phenomenon of the flow of solvent molecules through a semipermeable membrane from pure solvent to the solution is known as osmosis.

Semipermeable membranes can be natural such as pig's bladder or parchment or can be synthetic such as cellophane. These membranes appear to be continuous sheets or films, yet they contain a network of submicroscopic holes or pores. **Semipermeable membrane** is the membrane which allows solvent molecules like water to pass through their holes but binds the passage for molecules of solute like salt.

If semipermeable membrane is placed between the pure solvent and solution as shown in the figure, the solvent molecules will flow through the membrane from pure solvent to the solution.

This process of the flow of the solvent is known as osmosis.



Level of solution rises in the thistle funnel due to osmosis of solvent

If the osmosis takes place between the solutions of different concentrations, then solvent molecules will move from the solution of low solute concentration to that of higher solute concentration. The flow will continue till the equilibrium is attained.

Examples of Osmosis

The examples of osmosis are :

(i) A raw mango placed in concentrated salt solution loses water *via* osmosis and shrivel into pickle.

(ii) Wilted flowers revive when placed in fresh water through osmosis.

(iii) A carrot that has become limp because of water loss into the atmosphere can be placed into the water making it firm once again through osmosis.

(iv) Through osmosis, blood cell collapse due to loss of water when placed in water containing more than 0.9% (mass/volume) salt solution.

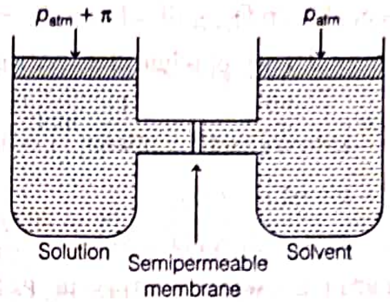
(v) People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. This resulting puffiness or swelling is called edema.

(vi) Water movement from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis.

(vii) The preservation of meat by salting and of fruits by adding sugar protects against bacterial action. Through the process of osmosis, a bacterium on salted meat or sugared fruits loses water, shrivels and dies.

Osmotic Pressure (π)

The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis, i.e. to stop the passage of solvent molecules through a semipermeable membrane into the solution. It is a colligative property as it depends upon the number of solute molecules and not on their nature.



The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis

Determination of Molar Mass of Solute

Osmotic pressure is proportional to the molarity (C) of the solution at a given temperature (T).

Thus, $\pi \propto C, \pi = CRT$ (For dilute solution)

where, π is the osmotic pressure and R is the gas constant.

But $C = \dfrac{n_2}{V}$ and $n_2 = \dfrac{W_2}{M_2}$

where, n_2 is the number of moles of solute dissolved in V L of solution, W_2 is the weight of solute and M_2 is its molar mass.

Therefore, $$\pi = \frac{W_2RT}{VM_2}$$

So, $$M_2 = \frac{W_2RT}{V\pi}$$

Measurement of osmotic pressure provides another method of determining molar masses of solutes. This method is widely used to determine molar masses of proteins, polymers and other macromolecules.

Advantages of Osmotic Pressure Method

(i) The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and the molarity of the solution is used instead of molality.

(ii) As compared to other colligative properties, its magnitude is large even for very dilute solutions. The technique of osmotic pressure for the determination of molar mass of solutes is particularly useful for biomolecules as they are generally not stable at higher temperatures and polymers have poor solubility. Osmotic pressure is measured by Berkeley and Hartley's method.

EXAMPLE |4| Calculate the osmotic pressure (in pascals) exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185000 in 450 mL of water at 37°C.

NCERT Intext

Sol. From the relation, $\pi = CRT = \dfrac{n}{V}RT$, we can find the value of π.

Mass of polymer = 1.0 g

Here, number of moles of solute dissolved (n)

$$= \frac{1.0 \text{ g}}{185000 \text{ g mol}^{-1}} = \frac{1}{185000} \text{ mol}$$

$$V = 450 \text{ mL} = 0.450 \text{ L}$$

$$T = 37°C = 37 + 273 = 310 \text{ K}$$

$$R = 8.314 \text{ kPa L K}^{-1} \text{ mol}^{-1} = 8.314 \times 10^3 \text{ Pa L K}^{-1}\text{mol}^{-1}$$

Substituting these values, we get

$$\pi = \frac{1}{185000} \text{ mol} \times \frac{1}{0.45 \text{ L}} \times 8.314 \times 10^3 \text{ Pa L K}^{-1}\text{mol}^{-1} \times 310 \text{ K} = 30.96 \text{ Pa}$$

Types of Solution on the Basis of Osmotic Pressure

There are three types of solutions on the basis of concentration and hence the applied osmotic pressure:

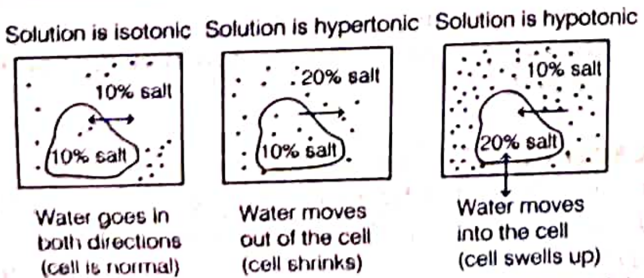
(i) **Isotonic solution** Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. There is no osmosis between these two solutions as they have same molar concentration.

e.g. The osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously.

(ii) **Hypertonic solution** A solution having more osmotic pressure than the other solution is called hypertonic solution.

e.g. If we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, then water will flow out of the cells and they would shrink. This process is called **plasmolysis**.

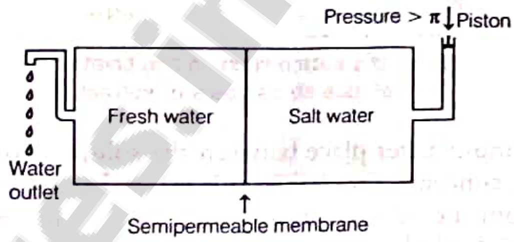
(iii) **Hypotonic solution** A solution having less osmotic pressure than the other solution is called hypotonic solution. e.g. If the salt concentration is less than 0.9% (mass/volume) sodium chloride, then water will flow into the cells and they would swell, if placed in this solution.



Transportation of water molecules (i.e. osmosis) in cases when cells are kept in different solutions

Reverse Osmosis and Water Purification

The direction of osmosis can be reversed, if a pressure larger than the osmotic pressure is applied to the solution side. Now, the pure solvent flows out of the solution through semipermeable membrane. This phenomenon is called reverse osmosis. This method is used in desalination to get salt free-water from sea water as shown in the figure.



Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution

When a pressure higher than the osmotic pressure of the sea water is applied, pure water passes through the semipermeable membrane leaving dissolved salt ions and other impurities behind.

The pressure required for the reverse osmosis is quite high. Variety of polymer membrane is available for this purpose. The most commonly used semipermeable membrane is that of cellulose acetate. This method of purification is boon for the regions where fresh water is scarcely available.

ABNORMAL MOLAR MASS

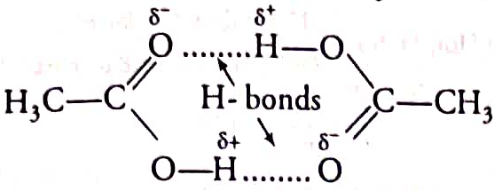
Ionic compounds when dissolved in water dissociates into cations and anions, e.g. one mole of KCl (74.5 g) in water dissociates into K^+ and Cl^- ions. Molecules of acetic acid or benzoic acid dimerise (associate) in benzene due to H-bonding. We have studied that the colligative properties help us to calculate the molar masses of solutes. But in case of association or dissociation of compounds, molar masses determined by these methods do not agree with theoretical value.

Such molar masses that are either lower or higher than the expected or normal values are called abnormal molar masses. Case of association or dissociation of compounds is described as:

Association of molecules leads to decrease in the number of particles in solution resulting in a decrease in the value of colligative properties.

Colligative properties are inversely related to molar mass of a compound. Therefore, higher value is obtained for molar mass than normal values, e.g. ethanoic acid in benzene undergoes dimerisation, it shows a molar mass of 120 (normal molar mass = 60).

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$



Dimerisation of acetic acid,

Dissociation of molecules leads to increase in the number of particles in solution resulting in an increase in the value of colligative properties. Due to this, lower value is obtained for molar mass than normal values, e.g. potassium chloride in water dissociates into K^+ and Cl^- ions and it shows a molar mass of 37.25 (normal molar mass = 74.5).

$$KCl \rightleftharpoons K^+ + Cl^-$$

van't Hoff derived a factor to deal with this abnormality in molar masses (or to deal with the extent of association and dissociation), which is discussed below.

van't Hoff Factor (i)

In 1880, van't Hoff introduced a factor i, known as van't Hoff factor to account for the extent of dissociation or association. It is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property.

$$i = \frac{\text{Normal (calculated) molar mass}}{\text{Observed (abnormal) molar mass}}$$

$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

$$\text{Colligative property} \propto \frac{1}{\text{Molar mass}}$$

In association, observed molar mass being more than the normal, so i has a value less than one ($i < 1$).

In dissociation, observed molar mass has lesser value than normal, so i is more than one ($i > 1$).

e.g. The value of i for ethanoic acid (acetic acid) in benzene is nearly 0.5 while for aqueous KCl, NaCl and $MgSO_4$ solution, it is nearly 2. The value of i for K_2SO_4 is nearly 3.

$$i = \frac{\text{Observed colligative property}}{\text{Normal (calculated) colligative property}}$$

Modified forms of Colligative Properties

Due to inclusion of van't Hoff factor, the modified forms of colligative properties are:

Relative lowering of vapour pressure, $\frac{\Delta p}{p^\circ} = i\chi_2$

or $$\frac{p_1^\circ - p_1}{p_1^\circ} = i \cdot \frac{n_2}{n_1}$$

Elevation in boiling point, $\Delta T_b = iK_b m$

Depression in freezing point, $\Delta T_f = iK_f m$

Osmotic pressure, $\pi = iCRT$ or $\frac{in_2RT}{V}$

EXAMPLE |5| Determine the amount of $CaCl_2$ ($i = 2.47$) dissolved in 2.5 L of water such that its osmotic pressure is 0.75 atm at 27°C. **NCERT**

> First calculate the moles of $CaCl_2$ by applying van't Hoff equation, $\pi = iCRT$ and $C = \frac{n_B}{V}$
>
> Then, calculate the amount of $CaCl_2$ by multiplying the moles with molar mass.

Sol From, $\pi = iCRT = i\frac{n}{V}RT$ or $n = \frac{\pi \times V}{i \times R \times T}$

Here, $\pi = 0.75$ atm; $V = 2.5$ L, $i = 2.47$;

$T = 300$ K $(27 + 273)$;

$R = 0.0821$ L atm $K^{-1} mol^{-1}$

$$\Rightarrow \quad n = \frac{0.75 \text{ atm} \times 2.5 \text{ L}}{2.47 \times 0.0821 \text{ L atm K}^{-1}\text{mol}^{-1} \times 300 \text{ K}}$$

$= 0.0308$ mol

Molar mass of $CaCl_2 = 40 + 2 \times 35.5 = 111$ g mol^{-1}

$\therefore$ Amount of $CaCl_2$ dissolved $= n \times M$

$= 0.0308 \times 111$ g $= 3.42$ g

Degree of Dissociation and Association

Using van't Hoff factor, the extent a degree of dissociation or association can be calculated.

Degree of dissociation It is defined as the fraction of the total substance that undergoes dissociation.

$$\alpha \text{ (degree of dissociation)} = \frac{(i-1)}{(n-1)}$$

Degree of association It is defined as the fraction of the total substance which exists in the form of associated molecules.

$$\alpha \text{ (degree of association)} = \frac{(1-i)}{\left(1 - \frac{1}{n}\right)}$$

If $i = 1$, it means solute behaves normally.

If $i = \frac{1}{2}$, it means solute is dimer.

If $i = \frac{1}{4}$, it means solute is tetra-atomic, e.g. P_4.

If $i = \frac{1}{8}$, it means solute is octa-atomic, e.g. S_8.

If $i > 1$, it means solute undergoes dissociation.

If $i < 1$, it means solute undergoes association.

EXAMPLE |6| A 0.5% aqueous solution of KCl was found to be freeze at $-0.24°C$. Calculate the van't Hoff factor and degree of dissociation of the solute at this concentration. (K_f for water = 1.86 K kg mol^{-1}).

Sol. Given, $K_f = 1.86 \text{K kg mol}^{-1}, W_2 = 0.5 \text{ g}, W_1 = 100 \text{ g}$,

$\Delta T_f = 0.24°C$

$$\text{Observed molecular mass of KCl} = \frac{1000 \times K_f \times W_2}{\Delta T_f \times W_1}$$

$$= \frac{1000 \times 1.86 \times 0.5}{0.24 \times 100} = 38.75$$

Normal molecular mass of KCl = 38.75 + 35.5 = 74.25

$$\text{van't Hoff factor} = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

$$i = \frac{74.25}{38.75} = 1.92$$

$$\underset{(1-\alpha)}{KCl} \rightleftharpoons \underset{\alpha}{K^+} + \underset{\alpha}{Cl^-}$$

Total number of particles $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

$i = 1 + \alpha \quad 1.92 = 1 + \alpha$

So, $\alpha = 1.92 - 1 = 0.92$, i.e. 92% dissociated.

| TOPIC PRACTICE 4 |

OBJECTIVE Type Questions

1. Colligative properties depend on .... **NCERT Exemplar**
   (a) the nature of the solute particles dissolved in solution
   (b) the number of solute particles in solution
   (c) the physical properties of the solute particles dissolved in solution
   (d) the nature of solvent particles

2. 12 g urea was dissolved in 1 L water and 68.4 g sucrose was dissolved in 1 L of water. Expected depression in vapour pressure of urea will be
   (a) more than that of sucrose solution
   (b) less than that of sucrose solution
   (c) double than that of sucrose solution
   (d) equal to sucrose solution

3. The unit of ebullioscopic constant is **NCERT Exemplar**
   (a) K kg mol^{-1} or K (molality)$^{-1}$
   (b) mol kg K^{-1} or K^{-1} (molality)
   (c) kg mol^{-1} K^{-1} or K^{-1} (molality)$^{-1}$
   (d) K mol kg^{-1} or K (molality)

4. Which of the following aqueous solutions should have the highest boiling point? **NCERT Exemplar**
   (a) 1.0 M NaOH
   (b) 1.0 M Na_2SO_4
   (c) 1.0 M NH_4NO_3
   (d) 1.0 M KNO_3

5. What happens to freezing point of benzene when naphthalene is added? **NCERT Exemplar**
   (a) Increases
   (b) Decreases
   (c) Remains unchanged
   (d) First decreases and then increases

6. The freezing point of a 0.2 molal solution of a non-electrolyte in water is **CBSE 2021 (Term I)**
   (K_f for water = 1.86 K kg mol^{-1})
   (a) $-$ 0.372°C (b) $-$ 1.86°C
   (c) + 0.372°C (d) + 1.86°C

7. How much ethyl alcohol must be added to 1 litre of water so that the solution will freeze at $-$ 14°C? (K_f for water = 1.86°C/mol), **CBSE SQP (Term I)**
   (a) 7.5 mol (b) 8.5 mol (c) 9.5 mol (d) 10.5 mol

8. The osmotic pressure of a solution increases if **CBSE 2021 (Term I)**
   (a) the volume of the solution increased
   (b) the number of solute molecules is increased
   (c) temperature is decreased
   (d) solution constant (R) is increased

9. At a given temperature, osmotic pressure of a concentrated solution of a substance .... **NCERT Exemplar**
   (a) is higher than that of a dilute solution
   (b) is lower than that of a dilute solution
   (c) is same as that of a dilute solution
   (d) cannot be compared with osmotic pressure of dilute solution

10. In which of the following cases blood cells will shrink? **CBSE SQP (Term I)**
    (a) When placed in water containing more than 0.9% (mass/ volume) NaCl solution
    (b) When placed in water containing less than 0.9% (mass /volume) NaCl solution
    (c) When placed in water containing 0.9% (mass/volume) NaCl solution
    (d) When placed in distilled water

VERY SHORT ANSWER Type Questions

11. Explain boiling point elevation constant for a solvent. **All India 2012; Foreign 2012**

Or

Define molal elevation constant, K_b. **Delhi 2014**

12. Will the depression in freezing point be same or different, if 0.1 mole of sugar or 0.1 mole of glucose is dissolved in 1 L of water?

13. It is advised to add ethylene glycol to water in car radiator while driving in hill station. Why?

14. Define the term osmotic pressure. **All India 2013; Delhi 2010 C, 2009**

15. What are isotonic solutions? **All India 2014**

16. What happens when we place the blood cell in water (hypotonic solution)? Give reason. **All India 2015**

17. State the condition for reverse osmosis. **All India 2020**

18. What will be the value of van't Hoff factor for a dilute solution of K_2SO_4 in water?

SHORT ANSWER Type I Questions

19. Define the following terms:
    (i) Colligative properties
    (ii) Molality (m) **Delhi 2017**

20. A glucose solution which boils at 101.04°C at 1 atm. What will be relative lowering of vapour pressure of an aqueous solution of urea which is equimolal to given glucose solution? (Given: K_b for water is 0.52 K kg mol^{-1}) **CBSE SQP 2021**

21. Explain why on addition of 1 mole of glucose to 1 litre of water, the boiling point of water increases? **Delhi 2017 C**

22. Explain, why on addition of 1 mole of NaCl to 1 L of water, the boiling point of water increases, while addition of 1 mole of methyl alcohol to 1 L of water decreases its boiling point? **NCERT Exemplar**

23. An aqueous solution of sodium chloride freezes below 273 K. Explain the lowering in freezing point of water with the help of a suitable diagram. **Delhi 2013 C**

24. Calculate the freezing point of a solution containing 60 g of glucose (Molar mass = 180 g mol^{-1}) in 250 g of water. (K_f of water = 1.86 Kkg mol^{-1}) **CBSE 2018**

25. Arrange the depression in freezing point of water observed for the same molar concentrations of acetic acid, trichloroacetic acid and trifluoroacetic acid. Explain this order as well. **NCERT; Delhi 2008 C**

26. How does sprinkling of salt help in clearing the snow covered roads in hilly areas? Explain the phenomenon involved in the process. **NCERT Exemplar**

27. Why do doctors advise gargles by saline water in case of sore throat?

28. Calculate the mass of a non-volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g of octane to reduce its vapour pressure to 80%. **NCERT**

29. Vapour pressure of water at 293 K is 17.535 mm of Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water. **NCERT**

30. 18 g of glucose, $C_6H_{12}O_6$ (molar mass = 180 g mol^{-1}) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil? (K_b for water = 0.52 K kg mol^{-1}, boiling point of pure water = 373.15 K). **Delhi 2013**

31. Calculate the mass of compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K. (K_f = 5.12 K kg mol^{-1}) **All India 2014**

32. The molecular masses of polymers are determined by osmotic pressure method and not by measuring other colligative properties. Give two reasons. **All India 2011C**

33. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 L of water at 25°C, assuming that it is completely dissociated. **Delhi 2013; NCERT**

34. At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration? **All India 2019, NCERT**

35. When kept in water, raisin swells in size. Name and explain the phenomenon involved with the help of a diagram. Give three applications of the phenomenon. **NCERT Exemplar**

36. Define the following terms:
 (i) Abnormal molar mass
 (ii) van't Hoff factor **Delhi 2017**
Delhi 2012; All India 2012, 2009

37. How many grams of KCl should be added to 1 kg of water to lower its freezing point to $-8.0°C$ (K_f for water = $1.86°C$ kg mol^{-1}).

SHORT ANSWER Type II Questions

38. Give reasons for the following: **CBSE 2018**
 (a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers.
 (b) Aquatic animals are more comfortable in cold water than in warm water.
 (c) Elevation of boiling point of 1 M KCl solution is nearly double than that of 1 M sugar solution.

39. At 25°C, the saturated vapour pressure of water is 3.165 kPa (23.75 mm of Hg). Find the saturated vapour pressure of a 5% aqueous solution of urea (carbamide) at the same temperature. (Molar mass of urea = 60.05 g mol^{-1}). **Foreign 2012**

40. A solution is prepared by dissolving 10 g of non-volatile solute in 200 g of water. It has a vapour pressure of 31.84 mm Hg at 308 K. Calculate the molar mass of the solute.
(Vapour pressure of pure water at 308 K = 32 mm of Hg) **All India 2015**

41. Vapour pressure of pure water at 298 K is 23.8 mm of Hg. 50 g of urea (NH_2CONH_2) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering. **NCERT Intext**

42. 15.0 g of unknown molecular material is dissolved in 450 g of water. The resulting solution freezes at $-0.34°C$. What is the molar mass of the material?
(K_f for water = 1.86 K kg mol^{-1}) **All India 2012, 2010**

43. Calculate the mass of ascorbic acid (vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C. (K_f for acetic acid = 3.9 K kg mol^{-1}). **All India 2010 C; NCERT Intext**

44. The freezing point of a solution containing 5g of benzoic acid (M = 122 g mol^{-1}) in 35g of benzene is depressed by 2.94 K. What is the percentage of association?
(K_f for benzene = 4.9 K kg mol^{-1}) **All India 2020**

45. A 10% solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water, if freezing point of pure water is 273.15 K.
Given, molar mass of sucrose = 342 g mol^{-1} and molar mass of glucose = 180 g mol^{-1}
Delhi 2017, All India 2017

46. Two elements A and B form compounds having molecular formula AB_2 and AB_4. When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molal depression constant for benzene is 5.1 K kg mol^{-1}. Calculate atomic masses of A and B. **NCERT**

47. A solution containing 15g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution. **Delhi 201**

48. A solution of urea in water has a boiling point of 373.128 K. Calculate the freezing point of the same solution. (Given, for water K_f = 1.86 K kg mol^{-1} and K_b = 0.52 K kg mol^{-1})
Delhi 2010 C, 2009 C

(i) First, find molality of the solution by using the formula,
$$\Delta T_b = K_b m$$
(ii) Find ΔT_f by using the formula, $\Delta T_f = K_f m$
(iii) Find freezing point of the solution by using the formula, $T_f^{\circ} = T_f - \Delta T_f$

49. Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2 K. (K_f for water $= 1.86$ K kg mol^{-1}) **Delhi 2012**

50. Calculate the boiling point of solution when 4 g of $MgSO_4$ ($M = 120$ g mol^{-1}) was dissolved in 100 g of water assuming $MgSO_4$ undergoes complete ionisation.
(K_b for water $= 0.52$ K kg mol^{-1}) **All India 2016**

51. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated).
(Given : Molar mass of benzoic acid $= 122$ g mol^{-1}, K_f for benzene $= 4.9$ K kg mol^{-1}) **Delhi 2015**

52. The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be
(K_f for benzene $= 5.12$ K kg mol^{-1})

LONG ANSWER Type Questions

53. (i) Explain why on addition of 1 mol glucose to 1 litre water, the boiling point of water increases.
(ii) Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K.
Calculate the number of moles of CO_2 in 500 mL of soda water when packed under 2.53×10^5 Pa at the same temperature. **All India 2017 C**

54. A solution containing 30 g of a non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate
(i) molar mass of the solute.
(ii) vapour pressure of water at 298 K. **NCERT**

55. Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86$ K kg mol^{-1}. **NCERT**

56. (i) Define the following terms :
(a) Ideal solution
(b) Osmotic pressure
(ii) A 0.01 m aqueous solution of $AlCl_3$ freezes at -0.068°C. Calculate the percentage of dissociation.
[Given : K_f for water $= 1.86$ K kg mol^{-1}] **Delhi 2020**

57. 19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0°C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid. (K_f for water is 1.86 K kg mol^{-1}) **NCERT**

HINTS AND EXPLANATIONS

1. (b) Colligative properties depend upon number of solute particles in solution irrespective of their nature.

2. (d) Expected depression in vapour pressure $= \dfrac{n}{n+N}$
where, n and N is the number of moles of solute and solvent.
Depression in vapour pressure of urea solution
$$= \frac{12/60}{12/60 + 1/18} = 0.78$$
Depression in vapour pressure of sucrose solution
$$= \frac{68.4/342}{\dfrac{68.4}{342} + 1/18} = 0.78$$
Thus, depression in vapour pressure of both is equal.

3. (a) As we know from elevation in boiling point that
$$\Delta T_b = K_b m \Rightarrow K_b = \frac{\Delta T_b}{m}$$
$$\text{Unit of } K_b = \frac{\text{unit of } \Delta T_b}{\text{unit of } m} = \frac{\text{K}}{\text{molality}}$$
$$= \frac{\text{K}}{\text{mol kg}^{-1}} = \text{K mol}^{-1}\ \text{kg}$$

4. (b) As we know greater the value of van't Hoff factor higher will be the elevation in boiling point and hence higher will be the boiling point of solution.

Solution	van't Hoff factor (i)
1.0 M NaOH	2
1.0 M Na_2SO_4	3
1.0 M NH_4NO_3	2
1.0 M KNO_3	2

Hence, 1.0 M Na_2SO_4 has highest value of boiling point.

5. (*b*) Freezing point of a pure solvent decreases on addition of solute and hence, a solution of benzene and naphthalene has lower freezing point than the freezing point of pure benzene.

6. (*a*) Molality of solution $(m) = 0.2$ m

Molal freezing point depression constant $(K_f) = 1.86 \text{ K Kg mol}^{-1}$

Depression in freezing point $(\Delta T_f) = K_f \times m$

$$\Delta T_f = 1.86 \times 0.2$$
$$\Delta T_f = 0.372°C$$

Now, $\Delta T_f = T_f^{\circ} - T_f$

where, T_f° = freezing point of pure solvent

T_f = freezing point of solution.

$$0.372 = 0 - T_f$$

$\therefore$ $T_f = -0.372°C$

7. (*a*) $\Delta T_f = K_f \times m$

$$\Delta T_f = \frac{K_f \times n_B \times 1000}{w_A (\text{in ml})}$$

where, ΔT_f = depression in freezing point

K_f = molal depression constant

n_B = number of moles of solute

w_A = given mass of solvent.

$$\therefore \quad 14 = \frac{1.86 \times n_B \times 1000}{1000}$$
$$n_B = \frac{14 \times 1000}{1.86 \times 1000}$$
$$n_B = 7.5 \text{ mol}$$

8. (*b*) The osmotic pressure of a solution increases when the number of solute molecules increases. Higher the number of solute molecules, higher will be the osmotic pressure.

9. (*a*) According to definition of osmotic pressure we know that $\pi = CRT$. For concentrated solution C has higher value than dilute solution.

Hence, as concentration of solution increases osmotic pressure will also increase.

10. (*a*) If the blood cells are placed in the solution containing more than 0.9% (mass/volume) NaCl, then water will flow out of the cells and they would shrink.

11. We know that, $\Delta T_b = K_b m$

If $m = 1$, then $\Delta T_b = K_b$. Thus, boiling point elevation constant is equal to the elevation in boiling point, when 1 mole of a solute is dissolved in 1 kg of solvent. It is also called Ebullioscopic constant.

12. It will be same for both solutions because both are non-electrolytes and give same number of solute particles.

13. Ethylene glycol lowers the freezing point of water, therefore, water does not freeze in hill station.

14. The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis.

15. Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.

16. On placing the red blood cells in water containing less than 0.9% salt, i.e. hypotonic solution, then due to osmosis, water molecules move into blood cells through the cell wall. As a result, blood cells swell and may even burst.

17. Pressure applied on the solution should be larger than osmotic pressure.

18. It is 3 because it gives 3 particles (ions) on dissociation.

$$K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$$

19. (i) Refer to text on page 25. (ii) Refer to text on page 4.

20. Given, $T_2 = 101.04°C$ and $K_b = 0.52 \text{ K kg mol}^{-1}$

We know that,

$$\Delta T_b = K_f m$$
$$\Delta T_b = T_2 - T_1 = 101.04 - 100 = 1.04°C$$

Using 1

or $m = \frac{\Delta T_b}{K_f} = \frac{1.04}{0.52} = 2$

Relative lowering of vapour pressure $= X_2$

Relative lowering of vapour pressure $= \frac{n_2}{n_1 + n_2}$

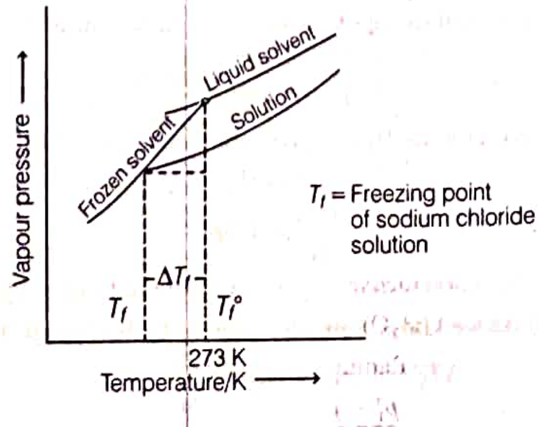
$$= \frac{2}{2 + 55.5} = \frac{2}{57.5} = 0.034 \text{ atm}$$

21. Vapour pressure of the solvent decreases in the presence of non-volatile solute (glucose) hence boiling point increases.

22. NaCl is a non-volatile solute. So, its addition to water lowers the vapour pressure of water. Hence, boiling point of water (solution) increases. Whereas methyl alcohol is more volatile than water. So, its addition to water increases the total vapour pressure of the solution. It results in decrease of boiling point of water.

23. When a non-volatile solute is added to a solvent, the freezing point of the solution is always lower than that of pure solvent as the vapour pressure of the solvent decreases in the presence of non-volatile solute.

Plot for the lowering in freezing point of water when NaCl is added to it is shown below



24. Molality of solution, $m = \frac{w_2}{M_2} \times \frac{1000}{w_1}$ ...(i)

where, w_2 weight of glucose = 60 g

M_2 molar mass of glucose = 180 g

w_1 weight of solvent (water) = 250 g

Putting value in Eq. (i) $= \frac{60 g}{180 g} \times \frac{1000 g}{250 g}$

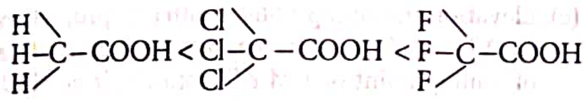
Molality $m = 1.33$

Now, $\Delta T_f = K_f m$, $K_f = 1.86 \text{K kg mol}^{-1}$

$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 1.33 \text{ m} = 2.47 \text{ K}$

25. The depression in freezing point is in the order:

Acetic acid < trichloroacetic acid < trifluoroacetic acid



Fluorine has the highest electron withdrawing inductive effect, so trifluoroacetic acid is the strongest acid and acetic acid is the weakest acid. Therefore, trifluoroacetic acid ionises to the greater extent and acetic acid ionises to the minimum extent. Greater the number of ions produced, greater is the depression in freezing point.

26. When salt is spread over snow covered roads, solution of salt and water is formed and as a result, depression in freezing point of water occurs. At the ambient temperature, snow starts melting and it helps in clearing the roads.

27. Sore throat is caused by viral and bacterial infection. When we gargle with salt water, there is a higher salt concentration than that of the infected cells. Through osmosis, water comes out of bacterial cells and infected cells thus, killing the pathogens and causing relief.

28. Here, $p = 80\%$ of $p_1^\circ = 0.80 p_1^\circ$

Number of moles of solute $(n_2) = \frac{W_2}{40}$ mol

Number of moles of solvent (octane) (n_1)

$$= \frac{114 \text{ g}}{114 \text{ g mol}^{-1}} = 1 \text{ mol}$$

($\because$ As molar mass of $C_8H_{18} = 114 \text{ g mol}^{-1}$)

Now, $\frac{p_1^\circ - p}{p_1^\circ} = \chi_2 = \frac{n_2}{(n_1 + n_2)}$

$\therefore \frac{p_1^\circ - 0.80 p_1^\circ}{p_1^\circ} = \frac{(W_2/40)}{(W_2/40 + 1)}$

$0.2\left(\frac{W_2}{40} + 1\right) = \frac{W_2}{40}$ or $\frac{0.8 W_2}{40} = 0.2$

or $W_2 = 10 \text{ g}$

29. Here, $p^\circ = 17.535$ mm of Hg, $W_2 = 25$ g, $W_1 = 450$ g

For solute (glucose, $C_6H_{12}O_6$), $M_2 = 180 \text{ g mol}^{-1}$

For solvent (H_2O), $M_1 = 18 \text{ g mol}^{-1}$

According to Raoult's law,

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{n_2}{n_1 + n_2}$$

or $\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{n_2}{n_1} = \frac{W_2/M_2}{W_1/M_1}$ (for dilute solution)

or $\frac{17.535 - p_1}{17.535} = \frac{W_2 M_1}{W_1 M_2}$

$\frac{17.535 - p_1}{17.535} = \frac{25 \times 18}{450 \times 180} = \frac{25}{4500} = 0.00556$

or $= 17.535 - p_1 = 0.09749$

$p_1 = 17.4375$ mm of Hg ≈ 17.44 mm of Hg

30. Given,

W_a = weight of H_2O (solvent) = 1 kg

W_b = weight of $C_6H_{12}O_6$ (glucose, solute) = 18 g

$T_b^\circ = 373.15$ K, $K_b = 0.52 \text{ K kg mol}^{-1}$

M_b = molar mass of solute (glucose) = 180 g mol^{-1}

$$\Delta T_b = \frac{K_b \times 1000 \times W_b}{M_b \times W_a}$$

$$= \frac{(0.52 \text{ K kg mol}^{-1}) \times 1000 \times 18 \text{ g}}{(180 \text{ g mol}^{-1}) \times 1000 \text{ g}}$$

$$= \frac{9360}{180000} = 0.052 \text{ K}$$

As we know that, $\Delta T_b = T_b - T_b^\circ$

$0.052 = T_b - 373.15$

$T_b = 373.15 + 0.052 = 373.202$ K

≈ 373.20 K (approx.)

31. Given that, $K_f = 5.12 \text{ K kg mol}^{-1}$

Mass of benzene, $W_1 = 75$ g

Depression in freezing point,

$\Delta T_f = 0.48$ K, $M_2 = 256 \text{ g mol}^{-1}$

If W_2 is the mass of compound,

Then, $\Delta T_f = \frac{K_f \times W_2 \times 1000}{W_1 \times M_2}$

(where, M_2 is molar mass of compound)

or $0.48 = \frac{5.12 \times W_2 \times 1000}{75 \times 256}$

$\therefore W_2 = \frac{0.489 \times 75 \times 256}{5.12 \times 1000} = 1.8$ g

32. The osmotic pressure method has the advantage over other methods because

(i) pressure measurement is around the room temperature and the molarity of the solution is used instead of molality.

(ii) its magnitude is larger as compared to other colligative properties even for very dilute solutions.

33. K_2SO_4 dissolved = 25 mg = 0.025 g

Volume of solution = 2 L

$T = 25°C = 25 + 273 = 298$ K

Molar mass of $K_2SO_4 = 2 \times 39 + 32 + 4 \times 16 = 174 \text{ g mol}^{-1}$

As, K_2SO_4 dissociates completely as follows

$K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$

i.e. ions produced = 3

$\therefore$ $i = 3$

$\therefore$ $\pi = iCRT = i\dfrac{n}{V}RT = i \times \dfrac{W}{M} \times \dfrac{1}{V} RT$

$= 3 \times \dfrac{0.025\text{ g}}{174\text{ g mol}^{-1}} \times \dfrac{1}{2\text{ L}} \times 0.0821\text{ L atm K}^{-1}\text{mol}^{-1} \times 298\text{ K}$

$= 5.27 \times 10^{-3}$ atm

34. $\pi = CRT = \dfrac{n}{V}RT = \dfrac{W_2 \times RT}{M_2 \times V}$

For both solutions, R, T and V are constant.

$\therefore$ In the first case, ($M_2 = 180$ for glucose)

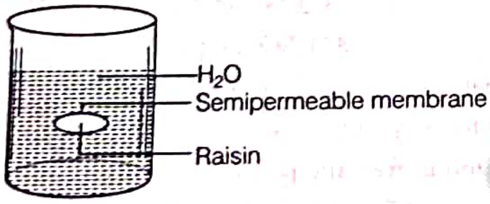
$$4.98 = \frac{36}{180} \times \frac{R \times 300}{V} \quad \text{...(i)}$$

In the second case, $1.52 = \dfrac{W_2}{M_2 V} \times R \times 300$ ...(ii)

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{W_2}{M_2 V} \text{ or } C = 0.061 \text{ mol L}^{-1}$$

35. This phenomenon is called endoosmosis, i.e. movement of water inside the raisin and shown with the help of diagram as:



The process of osmosis is of immense biological as well as industrial importance. It is evident from the following examples:

(i) Movement of water from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis.

(ii) Preservation of meat against bacterial action by the addition of salt.

(iii) Preservation of fruits against bacterial action by adding sugar. Bacterium in canned fruit loses water through the process of osmosis and become inactive.

(iv) Reverse osmosis is used in desalination of water.

36. Refer to text on pages 30 and 31.

37. $KCl \longrightarrow K^+ + Cl^-$

1 mole of KCl gives 2 moles of particles

$\therefore$ $i = 2$

$\Delta T_f = iK_f m$

Here, $\Delta T_f = T_f^\circ - T_f = 0 - (-8.0) = 8°C$

$$m = \frac{8}{2 \times 1.86} = 2.15 \text{ mol/kg}$$

Molar mass of KCl is $(39 + 35.5) = 74.5$ g mol^{-1}

As, $m = \dfrac{W_{KCl}}{M_{KCl} \times W_{H_2O}\text{ (kg)}} = 2.15$ mol/kg

Therefore, $W_{KCl} = m \times M_{KCl} \times W_{H_2O}$ (kg)

$= 2.15 \times 74.5 \times 1 = 160.2$ g per kg

$\therefore$ 160.2 g of KCl should be added to 1 kg of water.

38. (a) The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and the molarity of the solution is used instead of molality.

(b) Oxygen is present in dissolved state in water. As per Henry's law when temperature rises solubility of a gas decreases in solvent, it means solubility of oxygen in warm water is less than cold water. This makes aquatic species respirate comfortably in cold water.

(c) Elevation in boiling point is directly proportional to 'i'. $\Delta T_b \propto i$. Now as given in the question, elevation of boiling point of 1 M KCl solution is nearly double than that of 1 M sugar solution. It is because KCl being ionic, dissociates into K^+ and Cl^- and therefore it's van't Hoff factor, i is 2 whereas for sugar van't Hoff factor is 1 as it does not undergoes such a dissociation.

39. $\dfrac{p_1^\circ - p_1}{p_1^\circ} = \chi_2 = \dfrac{n_2}{n_1}$ [for dilute solution, $n_2 << n_1$]

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{W_2 \times M_1}{M_2 \times W_1}$$

Given, $p_1^\circ = 3.165$ kPa, $W_2 = 5$ g, $W_1 = 95$ g

$M_2 = 60.05$ g mol^{-1}, $M_1 = 18$ g mol^{-1}

$$\frac{3.165 - p_1}{3.165} = \frac{5 \times 18}{60.05 \times 95} = 0.0158$$

$3.165 - p_1 = 0.050$ or $p_1 = 3.115$ kPa

40. Molar mass of solute = 180 g mol^{-1}.

Refer to example 1 on page 26.

41. Here, $p^\circ = 23.8$ mm of Hg, $W_2 = 50$ g, $W_1 = 850$ g

For solute, urea (NH_2CONH_2), $M_2 = 60$ g mol^{-1}

For solvent (H_2O), $M_1 = 18$ g mol^{-1}

According to Raoult's law, $\dfrac{p_1^\circ - p_1}{p_1^\circ} = \dfrac{n_2}{n_1 + n_2}$

or $\dfrac{p_1^\circ - p_1}{p_1^\circ} = \dfrac{n_2}{n_1} = \dfrac{W_2/M_2}{W_1/M_1}$

(for dilute solution, $n_1 + n_2 \simeq n_1$)

or $1 - \dfrac{p_1}{p_1^\circ} = \dfrac{W_2 \times M_1}{W_1 \times M_2}$

Substituting the values, we get

$$1 - \frac{p_1}{23.8} = \frac{50}{60} \times \frac{18}{850} = \frac{3}{170} \Rightarrow \frac{p_1}{23.8} = 1 - \frac{3}{170} = \frac{167}{170}$$

$$p_1 = \frac{167 \times 23.8}{170} = \frac{3974.6}{170} = 23.38 \text{ mm of Hg}$$

Relative lowering of vapour pressure

$$= \frac{p_1^\circ - p_1}{p_1^\circ} = \frac{23.80 - 23.38}{23.80} = \frac{0.42}{23.80} = 0.018$$

42. $$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

Given, $W_1 = 450\,g$, $W_2 = 15.0\,g$

$\Delta T_f = 0.34\,K$, $K_f = 1.86\,K\,kg\,mol^{-1}$

$$\Rightarrow \quad M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1}$$

$$M_2 = \frac{1.86\,K\,kg\,mol^{-1} \times 15\,g \times 1000}{0.34\,K \times 450\,g} = 182.35\,g\,mol^{-1} \quad (2)$$

43. Lowering in melting point $(\Delta T_f) = 1.5°C$

Mass of solvent (CH_3COOH), $W_1 = 75\,g$

Molar mass of solvent (CH_3COOH), $M_1 = 60\,g\,mol^{-1}$

[as $CH_3COOH = 12 + 3 + 12 + 16 + 16 + 1 = 60$]

Molar mass of solute ($C_6H_8O_6$),

$M_2 = 72 + 8 + 96 = 176\,g\,mol^{-1}$

[as, $C_6H_8O_6 = 6 \times 12 + 8 \times 1 + 6 \times 16 = 176$]

For acetic acid, $K_f = 3.9\,K\,kg\,mol^{-1}$ [Given]

Applying the formula, $M_2 = \dfrac{1000 K_f W_2}{W_1 \Delta T_f}$, we get

$$W_2 = \frac{M_2 \times W_1 \times \Delta T_f}{1000 \times K_f}$$

$$= \frac{(176\,g\,mol^{-1})\,(75\,g)\,(1.5\,K)}{(1000)\,(3.9\,K\,kg\,mol^{-1})} = 5.077\,g$$

44. Let the degree of association of benzoic acid in benzene is α, then

$$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

	$2C_6H_5COOH$	$(C_6H_5COOH)_2$
Initial moles	1	0
Moles of equilibrium	$1-\alpha$	$\alpha/2$

$\therefore$ Total moles $= 1 - \alpha + \dfrac{\alpha}{2} = 1 - \dfrac{\alpha}{2}$ or $i = 1 - \dfrac{\alpha}{2}$

Now, depression in freezing point (ΔT_f) is

$$\Delta T_f = i\,K_f \cdot m \quad \text{...(i)}$$

$$\text{Molality } (m) = \frac{\text{number of moles of solute}}{\text{mass of solvent (kg)}} = \frac{5}{122} \times \frac{1000}{35}$$

Putting values in (i)

$$\therefore \quad 2.94 = 4.9 \times \left(1 - \frac{\alpha}{2}\right)\left(\frac{5}{122} \times \frac{1000}{35}\right) \Rightarrow \alpha = 0.9752$$

$\therefore$ Thus, the percentage of association = 97.52%

45. First, calculate the value of molality (m) of sucrose, using

$$m = \frac{W_{solute} \times 1000}{M_{solute} \times W_{solvent}}$$

then, calculate the cryoscopic constant (K_f) by using depression is freezing point, $\Delta T_2 = K_f m$.

Finally calculate the ΔT_f of glucose solution followed by freezing point of glucose solution $T_f = 273.15 - \Delta T_f$.

For sucrose solution,

Molality of sucrose solution $= \dfrac{W_2 \times 1000}{M_2 \times W_1}$

Given, $W_2 = 10\,g$, $W_1 = 90\,g$, $M_2 = 342\,g\,mol^{-1}$

$$\text{Molality } (m) = \frac{10}{342} \times \frac{1000}{90} = 0.324\ mol\ kg^{-1}$$

ΔT_f for sucrose solution $= 273.15\ K - 269.15\ K = 4K$

$$\Delta T_f = k_f m \qquad K_f = \frac{4}{0.324} K\,kg\,mol^{-1}$$

For glucose solution

$W_2 = 10\,g$, $W_1 = 90\,g$, $M_2 = 180\,g\,mol^{-1}$

$$\text{Molality } (m) = \frac{10}{180} \times \frac{1000}{90} = 0.617\ mol\ kg^{-1}$$

$\Delta T_f = K_f m$

$$\therefore\ \Delta T_f\ (\text{glucose}) = \frac{4}{0.324} \times 0.617 = 7.617$$

Hence, freezing point of glucose solution

$= 273.15\,K - 7.617\ K = 265.53\,K$

46. Applying the formula, $M_2 = \dfrac{1000 K_f W_2}{W_1 \times \Delta T_f}$

For AB_2, $M_{AB_2} = \dfrac{1000 \times 5.1 \times 1}{20 \times 2.3} = 110.87\ g\ mol^{-1}$

For AB_4, $M_{AB_4} = \dfrac{1000 \times 5.1 \times 1}{20 \times 1.3} = 196.15\ g\ mol^{-1}$

Suppose atomic masses of A and B are a and b respectively, then

Molar mass of $AB_2 = a + 2b = 110.87\ g\ mol^{-1}$ ...(i)

Molar mass of $AB_4 = a + 4b = 196.15\ g\ mol^{-1}$ ...(ii)

On subtracting Eq. (i) from Eq. (ii) gives

$2b = 85.28$

Therefore, $b = 42.64$

On substituting the value of b in Eq. (i), we get

$a + 2 \times 42.64 = 110.87$

or $a = 25.59$

Thus, atomic mass of $A = 25.59$ u,

Atomic mass of $B = 42.64$ u

47. Here, $W_1 = 15\,g$, $M_1 = 60\,g\,mol^{-1}$, $V_1 = 1\,L$

$M_2 = 180\,g\,mol^{-1}$, $V_2 = 1\,L$

$$\pi = CRT = \frac{W}{m}\frac{RT}{V}$$

For both solutions, π, R, T and V are same.

For urea solution, $\pi = \dfrac{15RT}{60}$

For glucose solution, $\pi = \dfrac{W_2 RT}{180}$

$$\because \quad \frac{15RT}{60} = \frac{W_2 RT}{180}$$

$$\therefore \quad W_2 = \frac{15 \times 180}{60} = 45\,g$$

48. Given, $T_b = 373.128$ K,

$K_f = 1.86$ K kg mol^{-1}, $K_b = 0.52$ K kg mol^{-1}

$\Delta T_b = 373.128 \text{ K} - 373 \text{ K} = 0.128 \text{ K}$

($\because T_b^\circ$ for water $= 373$ K)

$$\Delta T_b = K_b m \text{ or } m = \frac{\Delta T_b}{K_b} = \frac{0.128 \text{ K}}{0.52 \text{ Km}^{-1}}$$

$$\Delta T_f = K_f m$$

$$\Delta T_f = \frac{1.86 \text{ Km}^{-1} \times 0.128 \text{ K}}{0.52 \text{ Km}^{-1}} = 0.458 \text{ K}$$

49. $$\Delta T_f = \frac{K_f \times W_2 \times 1000}{W_1 \times M_2} \times i$$

Here, $M_2 = 74.5$, $K_f = 1.86$ K kg mol^{-1}, $W_1 = 1$ kg

$\Delta T_f = 2$ K

$$2 = \frac{1.86 \times W_2 \times 1000}{1000 \times 74.5} \times 2 = \frac{2 \times 74.5}{1.86 \times 2} = W_2$$

$W_2 = 40.05$ g

50. Given, weight of solute, $W_2 = 4$ g

weight of solvent, $W_1 = 100$ g

$i = 2$ (as $MgSO_4$ dissociates completely into 2 ions)

$$MgSO_4 \rightleftharpoons Mg^{2+} + SO_4^{2-}$$

$K_b = 0.52$ K kg mol^{-1} $\quad M_2 = 120$ g mol^{-1}

$\therefore$ The elevation in boiling point of solution,

$$\Delta T_b = \frac{i \times K_b \times W_2 \times 1000}{M_2 \times W_1}$$

where, i = van't Hoff factor

W_2 = weight of solute

W_1 = weight of solvent ,

M_2 = molar mass of solute

T_b° = boiling point of pure solvent

$$= \frac{2 \times 0.52 \times 4 \times 1000}{120 \times 100} = 0.346 \text{ K}$$

At boiling point of pure water is 100°C or 373 K.

$$T_b = \Delta T_b + T_b^\circ$$

$\therefore \quad T_b = 373 + 0.346 = 373.346$ K

51. The given quantities are :

$W_2 = 3.9$ g, $W_1 = 49$ g

$\Delta T_f = 1.62$ K, $K_f = 4.9$ K kg mol^{-1}

Apply van't Hoff equation, $\Delta T_f = i K_f \cdot m$

where, i = number of ions

$$\Delta T_f = \frac{i \cdot K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$\Rightarrow 1.62 \text{ K} = \frac{i \cdot 4.9 \text{ K kg mol}^{-1} \times 3.9 \text{ g} \times 1000}{122 \text{ g mol}^{-1} \times 49 \text{ g}}$$

$$i = \frac{1.62 \times 122 \times 49}{4.9 \times 3.9 \times 1000} = 0.51$$

As the value of $i < 1$ thus benzoic acid is an associated solute.

52. Let the degree of association of acetic acid (CH_3COOH) in benzene is α, then

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

Initial moles $\quad K \longrightarrow 1 \quad K \longrightarrow 0$

Moles at equilibrium $\quad 1-\alpha \quad \frac{\alpha}{2}$

$$\therefore \text{ Total moles} = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2} \text{ or } i = 1 - \frac{\alpha}{2}$$

Now, depression in freezing point (ΔT_f) is given as

$$\Delta T_f = i K_f m \quad \ldots\text{(i)}$$

where, K_f = molal depression constant or cryoscopic constant.

m = molality

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{weight of solvent (in kg)}} = \frac{0.2}{60} \times \frac{1000}{20}$$

Putting the values in Eq. (i)

$$\therefore \quad 0.45 = \left[1 - \frac{\alpha}{2}\right](5.12)\left[\frac{0.2}{60} \times \frac{1000}{20}\right]$$

$$1 - \frac{\alpha}{2} = \frac{0.45 \times 60 \times 20}{5.12 \times 0.2 \times 1000}$$

$$\Rightarrow \quad 1 - \frac{\alpha}{2} = 0.527 \Rightarrow \frac{\alpha}{2} = 1 - 0.527$$

$\therefore \quad \alpha = 0.946$

Thus, percentage of association = 94.6%

53. (i) Refer to text on page 26.

(ii) $l_{CO_2} = K_H X_{CO_2}$

$X_{CO_2} = p_{CO_2} / K_H$

$= 2.53 \times 10^5$ Pa$/ 1.67 \times 10^8$ Pa $= 1.51 \times 10^{-3}$

$n_{H_2O} = 500$ g$/ 18$ g/mol $= 27.77$ mol

Let $n_{CO_2} = n$ mol

Let $n_{CO_2} = n/(27.77 + n) = 1.51 \times 10^{-3}$

$n_{CO_2} = 1.51 \times 10^{-3} \times 27.77$ mol $= 0.042$ mol

54. (i) Suppose the molar mass of solute $= M$ g mol^{-1}

Number of moles of solute $(n_2) = \frac{30}{M}$ mol

Number of moles of H_2O

$$(n_1) = \frac{90 \text{ g}}{18 \text{ g mol}^{-1}} = 5 \text{ mol and } p_1 = 2.8 \text{ kPa}$$

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{n_2}{n_1 + n_2} \text{ and } \frac{p_1^\circ - 2.8}{p_1^\circ} = \frac{30/M}{5 + 30/M}$$

$$\text{or} \quad 1 - \frac{2.8}{p_1^\circ} = \frac{30/M}{5 + 30/M}$$

$$\text{or} \quad \frac{2.8}{p_1^\circ} = 1 - \frac{30/M}{5 + 30/M} = \frac{5}{5 + 30/M}$$

$$\text{or} \quad \frac{p_1^\circ}{2.8} = \frac{5 + 30/M}{5} = 1 + \frac{6}{M} \quad \ldots\text{(i)}$$

On adding 18 g of water, $n(H_2O) = 6$ mol

$(= 5 + 1 = 6$ mol$)$

Then, $p_1' = 2.9$ kPa

$$\therefore \quad \frac{p_1^\circ - 2.9}{p_1^\circ} = \frac{30/M}{6+30/M} \text{ or } 1 - \frac{2.9}{p_1^\circ} = \frac{30/M}{6+30/M}$$

$$\text{or} \quad \frac{2.9}{p_1^\circ} = 1 - \frac{30/M}{6+30/M} = \frac{6}{6+30/M}$$

$$\text{or} \quad \frac{p_1^\circ}{2.9} = \frac{6+30/M}{6} = 1 + \frac{5}{M} \quad \ldots\text{(ii)}$$

On dividing Eq. (i) by Eq. (ii), we get

$$\frac{2.9}{2.8} = \frac{1+6/M}{1+5/M}$$

$$\text{or } 2.9\left(1+\frac{5}{M}\right) = 2.8\left(1+\frac{6}{M}\right) \text{ or } 2.9 + \frac{14.5}{M} = 2.8 + \frac{16.8}{M}$$

$$\Rightarrow \quad M = 23 \text{ u}$$

(ii) Putting $M = 23$ in Eq. (i), we get

$$\frac{p_1^\circ}{2.8} = 1 + \frac{6}{23} = \frac{29}{23} \text{ or } p_1^\circ = \frac{29}{23} \times 2.8 = 3.53 \text{ kPa}$$

55. Molar mass of $CH_3CH_2CHClCOOH$

$$= 15 + 14 + 13 + 35.5 + 45 = 122.5 \text{ g mol}^{-1}$$

Number of moles of 10 g of $CH_3CH_2CHClCOOH$

$$n_2 = \frac{10}{122.5} \text{ mol} = 8.16 \times 10^{-2} \text{ mol}$$

$\therefore$ Molality of the solution (m)

$$= \frac{W_2 \times 1000}{M_2 \times W_1} = \frac{n_2 \times 1000}{W_1} = \frac{8.16 \times 10^{-2} \text{ mol}}{250 \text{ g}} \times 1000 \text{ g kg}^{-1}$$

$C = 0.3264$ mol kg^{-1}

If α is the degree of dissociation for $CH_3CH_2CHClCOOH$, then

$$CH_3CH_2CHClCOOH \rightleftharpoons CH_3CH_2CHClCOO^- + H^+$$

Initial conc.	C mol L^{-1}	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$\therefore \quad K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} \approx C\alpha^2$$

$$\text{or} \quad \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} = 0.065$$

To calculate van't Hoff factor

$$CH_3CH_2CHClCOOH \rightleftharpoons CH_3CH_2CHClCOO^- + H^+$$

Initial moles	1	0	0
Moles at equilibrium	$(1-\alpha)$	α	α

Total moles $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$i = \frac{1+\alpha}{1} = 1 + \alpha = 1 + 0.065 = 1.065$$

Therefore, $\Delta T_f = iK_f m = 1.065 \times 1.86 \times 0.3264 = 0.65°$

56. (i) (a) The solutions which obey Raoult's law over the entire range of concentration.

(b) It is the excess pressure that must be applied to a solution to prevent osmosis.

(ii) Given, Molality of $AlCl_3$ solution, $m = 0.01$ m

$T_f = -0.068$ °C, $K_f = 1.86$ K kg mol^{-1}

$$\Delta T_f = i \times K_f \times m \Rightarrow i = \frac{\Delta T_f}{K_f \times m}$$

$$i = \frac{0.068}{1.86 \times 0.01} \qquad [\because \Delta T_f = T_f^\circ - T_f]$$

$i = 3.65$

The dissociation of $AlCl_3$ can be shown as :

$$AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$$

Initially, let 1 mole of $AlCl_3$ is present. Hence,

$$AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$$

Initially	1 mol	0 mol	0 mol
At equilibrium	$(1-\alpha)$ mol	α mol	3α mol

(where, α = degree of dissociation)

Total number of moles at equilibrium

$= 1 - \alpha + \alpha + 3\alpha \Rightarrow (1 + 3\alpha)$

$AlCl_3$ is a weak electrolyte and for weak electrolytes,

$$i = \frac{\text{number of moles at equilibrium}}{\text{initial number of moles}}$$

$$i = \frac{1+3\alpha}{1} \Rightarrow 3.65 = \frac{1+3\alpha}{1}$$

$$3\alpha = 2.65 \Rightarrow \alpha = 0.8833$$

or percentage of dissociation is 88.33%.

57. Here, $W_2 = 19.5$ g, $W_1 = 500$ g,

$K_f = 1.86$ K kg mol^{-1}, $(\Delta T_f)_{obs} = 1.0°$

$$\therefore \quad M_2(\text{observed}) = \frac{1000 K_f W_2}{W_1 \Delta T_f}$$

$$= \frac{(1000 \text{ g kg}^{-1})(1.86 \text{ K kg mol}^{-1})(19.5 \text{ g})}{(500 \text{ g})(1.0 \text{ K})}$$

$$= 72.54 \text{ g mol}^{-1}$$

M_2 (calculated) for CH_2FCOOH

$$= 14 + 19 + 45 = 78 \text{ g mol}^{-1}$$

$$\text{van't Hoff factor } (i) = \frac{(M_2)_{cal}}{(M_2)_{obs}} = \frac{78}{72.54} = 1.0753$$

Suppose degree of dissociation at the given concentration is α. Then,

$$CH_2FCOOH \rightleftharpoons CH_2FCOO^- + H^+$$

Initial moles	C mol L^{-1}	0	0
Moles at equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Total moles $= C(1-\alpha) + C\alpha + C\alpha = C(1+\alpha)$

$$\therefore \quad i = \frac{C(1+\alpha)}{C} = 1 + \alpha$$

$$\text{or} \quad \alpha = i - 1 = 1.0753 - 1 = 0.0753$$

$$K_a = \frac{[CH_2FCOO]^- [H]^+}{[CH_2FCOOH]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Taking volume of the solution as 500 mL,

$$C = \frac{n}{V} = \frac{W_2}{M_{2(cal)}} \times \frac{1}{V} = \frac{19.5}{78} \times \frac{1}{500} \times 1000 = 0.5 \text{ M}$$

$$\therefore \quad K_a = \frac{C\alpha^2}{1-\alpha} = \frac{(0.5)(0.0753)^2}{1 - 0.0753} = 3.07 \times 10^{-3}$$

SUMMARY

- A solution is a homogeneous mixture of two or more substances i.e. one phase system.
- In a solution, there are three types of interaction
  Solvent—solvent   Solvent—solute   Solute—solute
- Expressing concentrations
  - % concentration by mass solution $= \dfrac{100 w_2}{w_1 + w_2}$
  - % concentration by mass solvent $= \dfrac{100 w_2}{w_1}$
  - ppm concentration $= \dfrac{10^6 w_2}{(w_1 + w_2)}$
  - ppb concentration $= \dfrac{10^9 w_2}{(w_1 + w_2)}$
  - Molarity $= \dfrac{1000\, w_2}{m_2 V}$, Normality $= \dfrac{1000\, w_2}{E_2 V}$
  - Formality $= \dfrac{\text{number gram formula weight}}{\text{volume of solution (in L)}}$
  - Molality $= \dfrac{1000 w_2}{m_2 w_1}$
  - Mole fraction $(\chi)_1 = \dfrac{n_1}{n_1 + n_2}$

  where, w_1 = mass of solvent (molar mass m_1, mol $= \dfrac{w_1}{m_1} = n_1$)

  w_2 = mass of solute (molar mass m_2, mol $= \dfrac{w_2}{m_2} = n_2$)

  V = volume of solution in mL, E_2 = equivalent mass of solute
- Concentration terms involving mass factors only are temperature independent.
- Normality of acid = molarity × basicity
- Normality of base = molarity × acidity
- Solubility of a gas in liquid is defined as the volume of the gas (in cm^3) which will dissolve in 1 cm^3 of the liquid to form a saturated solution at particular temperature and pressure.

  From Henry's law, solubility of gas $\propto p$.

  $$m \propto p \text{ or, } p = K_H \chi$$
- where, K_H = Henry's constant, χ = mole fraction
- Vapour pressure of mixture of two volatile liquids

  $$p_A = p_{A^\circ} \chi_A \;;\; p_B = p_{B^\circ} \chi_B$$

  $$p_{total} = p_{A^\circ}\chi_A + p_{B^\circ}\chi_B = p_A + p_B$$

  $$= p_{B^\circ} + (p_{A^\circ} - p_{B^\circ})\chi_A = p_{A^\circ} + (p_{B^\circ} - p_{A^\circ})\chi_B$$

  Mole fraction of the given component in vapour phase above liquid mixture $\chi_A' = \dfrac{p_{A^\circ}\chi_A}{p_{total}} = \dfrac{p_{A^\circ}\chi_A}{p_{A^\circ}\chi_A + p_{B^\circ}\chi_B}$
- If intermolecular attraction of $A - A$ or $B - B$ and $A - B$ are equal then solution of A and B is ideal. $\Delta H_{mix} = \Delta V_{mix} = 0$

  There is no deviation from Raoult's law.
- Intermolecular attraction $A - A$ or $B - B < A - B$ then vapour pressure of the mixture is less than the expected (theoretical value $= p_{A^\circ}\chi_A + p_{B^\circ}\chi_B$) value – a case of negative deviation from Raoult's law.

  $\Delta H_{mix} = -$ ve $\Delta V_{mix} = -$ ve.
- Intermolecular attraction $A - A$ or $B - B > A - B$, then vapour pressure of the mixture is more than the expected value – a case of positive deviation from Raoult's law.

  $\Delta H_{mix} = +$ ve $\Delta V_{mix} = +$ ve.
- Solutions showing deviations from Raoult's law cannot be separated into components by simple or fractional distillation and are called azeotropic mixture.
- Properties, whose values depend only on the concentration of solute particles in solution and not on the identity of the solute are called colligative properties. Examples are
  - Relative lowering of vapour pressure
  - Elevation is bp (ΔT_b)
  - Depression in freezing point (ΔT_f)
  - Osmotic pressure (π)
- Vapour pressure of solution containing non-volatile solute

  $$p_{solution} = p_{solvent} \times \chi_{solvent}$$
- Raoult's law for Relative lowering of vapour pressure $= \chi_{solute}$

  $$\frac{\Delta p}{p^\circ} = \chi_1 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \text{ for dilute solution}$$
- Elevation in boiling point $\Delta T_b = \dfrac{1000\, K_b w_2 (i)}{m_2 w_1}$ = molality × K_b × i

  where, K_b (molal elevation constant) $= \dfrac{RT_b^2}{1000 \Delta H_v}$

  R = gas constant T_b^0 = boiling point of solvent

  ΔH_v = latent heat of vaporisation (in heat unit per gram solvent)
- Depression in freezing point

  $$\Delta T_f = \frac{1000\, K_f w_2 (i)}{m_2 w_1} = \text{molality} \times K_f \times i$$

  K_f (molal depression constant) $= \dfrac{RM_1 T_f^2}{1000 \Delta H_f}$

  T_f° = freezing point of solvent

  ΔH_f = latent heat of fusion (in heat unit per gram solvent)
- Spontaneous flow of solvent from dilute solution (or pure solvent) into the concentrated solution through a semi permeable membrane is called osmosis. Pressure required to prevent osmosis is called osmotic pressure (π).

  $\pi_A = \pi_B$, A and B are isotonic

  $\pi_A > \pi_B$ A is hypertonic, B is hypotonic
- Osmotic pressure (π) $\pi = i \dfrac{n}{V} RT$

  where, n = number of moles of solute, V = volume of solution

  T = temperature, i = van't Hoff factor
- van't Hoff factor $i = [1 + (y - 1)x]$

  where, y = number of ions or molecules due to ionisation or association

  $i = 1$; when no change $i > 1$; when dissociation

  $i < 1$; when association

CHAPTER PRACTICE

OBJECTIVE Type Questions

1 29.2% (w/W) HCl stock solution has density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5 mol^{-1}. The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 M HCl is

(a) 5.0 mL
(b) 6.0 mL
(c) 8.0 mL
(d) 15.0 mL

2 Ratio of O_2 and N_2 in the air is 1 : 4. Find out the ratio of their solubilities in terms of mole fractions of O_2 and N_2 dissolved in water at atmospheric pressure and room temperature.

$$\begin{bmatrix} K_H(O_2) = 3.30 \times 10^7 \text{ torr} \\ K_H(N_2) = 6.60 \times 10^7 \text{ torr} \end{bmatrix}$$

(a) 1 : 2 (b) 2 : 1
(c) 1 : 1 (d) None of these

3 Which one of the following is not correct for an ideal solution?

(a) It must obey Raoult's law
(b) $\Delta H = 0$
(c) $\Delta V = 0$
(d) $\Delta H = \Delta V \neq 0$

4 Which of the following statements is false?

(a) Units of atmospheric pressure and osmotic pressure are the same
(b) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration
(c) The value of molal depression constant depends on nature of solvent
(d) Relative lowering of vapour pressure, is a dimensionless quantity

5 We have three aqueous solutions of NaCl labelled as '*A*', '*B*' and '*C*' with concentrations 0.1 M, 0.01 M and 0.001 M, respectively. The value of van't Hoff factor for these solutions will be in the order .... **NCERT Exemplar**

(a) $i_A < i_B < i_C$ (b) $i_A > i_B > i_C$
(c) $i_A = i_B = i_C$ (d) $i_A < i_B > i_C$

CASE BASED Questions

Case I

Boiling point or freezing point of liquid solution would be affected by the dissolved solids in the liquid phase. A soluble solid in solution has the effect of raising its boiling point and depressing its freezing point. The addition of non-volatile substances to a solvent decreases the vapour pressure and the added solute particles affect the formation of pure solvent crystals.

According to many researches the decrease in freezing point directly correlated to the concentration of solutes dissolved in the solvent. This phenomenon is expressed as freezing point depression and it is useful for several applications such as freeze concentration of liquid food and to find the molar mass of an unknown solute in the solution. Freeze concentration is a high quality liquid food concentration method where water is removed by forming ice crystals. This is done by cooling the liquid food below the freezing point of the solution's identity.

The freezing point depression is referred as a colligative property and it is proportional to the molar concentration of the solution (m), along with vapour pressure lowering, boiling point elevation, and osmotic pressure. These are physical characteristics of solutions that depend only on the identity of the solvent and the concentration of the solute. The characters are not depending on the solute's identity. **CBSE Question Bank**

The following questions are multiple choice questions. Choose the most appropriate answer :

6. When a non-volatile solid is added to pure water it will

(a) boil above 100°C and freeze above 0°C
(b) boil below 100°C and freeze above 0°C
(c) boil above 100°C and freeze below 0°C
(d) boil below 100°C and freeze below 0°C

7. Colligative properties are

(a) dependent only on the concentration of the solute and independent of the solvent's and solute's identity.
(b) dependent only on the identity of the solute and the concentration of the solute and independent of the solvent's identity.
(c) dependent on the identity of the solvent and solute and, thus on the concentration of the solute.
(d) dependent only on the identity of the solvent and the concentration of the solute and independent of the solute's identity.

8. Assume three samples of juices *A*, *B* and *C* have glucose as the only sugar present in them. The concentration of sample *A*, *B* and *C* are 0.1 M, .5 M and 0.2 M respectively. Freezing point will be highest for the fruit juice
(a) *A*
(b) *B*
(c) *C*
(d) All have same freezing point

9. Identify which of the following is a colligative property
(a) freezing point
(b) boiling point
(c) osmotic pressure
(d) All of these

Case II

When a non-volatile solute is added to a solvent, the freezing point of the formed solution is always lower than that of pure solvent. This difference in freezing point is known as depression in freezing point. If $\Delta T_f°$ is the freezing point temperature of pure solvent and T_f is the freezing point temperature of the solution when non-volatile solute is dissolved in it, then depression in freezing point (ΔT_f) is given by.

$$\Delta T_f = T_f° - T_f$$

For dilute solutions, $\Delta T_f = K_f m$

[where, m = molal concentration of the solution]

In the question that follow Assertion and Reason are given. Reason is purported to the explaination for Assertion. Study carefully and then mark your answers, according to the codes given below.

Marks your answer as :
(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

10 **Assertion** The freezing point of solution is always lower than that of pure solvent.
Reason Non-volatile solute decreases the vapour pressure of the solvent.

11 **Assertion** Depression in freezing point is depends upon K_f.
Reason It depends molality of solution.

12 **Assertion** Cryoscopic constant is also known as molal freezing point depression constant (K_f).
Reason It contains 100g of solvent for 1 molal solution.

Or **Assertion** The depression in freezing point of 5% glucose is water is 4.08.
Reason K_f is 13.962 K kg mol^{-1}.

13 **Assertion** K_f is not unit less.
Reason Unit of K_f is K kg mol^{-1}.

ASSERTION and REASON

■ *Directions (Q. Nos. 14-21) In the following questions, an Assertion (A) is followed by a corresponding Reason (R) Use the following keys to choose the appropriate answer.*
(a) Both (A) and (R) are correct, (R) is the correct explanation of (A).
(b) Both (A) and (R) are correct, (R) is not the correct explanation of (A).
(c) (A) is correct; (R) is incorrect.
(d) (A) is incorrect; (R) is correct.

14 **Assertion** (A) One molar aqueous solution has always higher concentration than one molal.
Reason (R) The molality of a solution depends upon the density of the solution whereas molarity does not.

15 **Assertion** (A) Aquatic species are more comfortable in cold water rather than in warm water. **CBSE SQP 2021**
Reason (R) Different gases have different K_H values at the same temperature.

16 **Assertion** (A) When scuba divers come towards surface, their capillaries get blocked which is painful and dangerous to life.
Reason (R) There occurred release of dissolved gases as the pressure decreases and leads to the formation of bubbles of nitrogen in the blood.

17 **Assertion** (A) Cryoscopic constant depends on nature of solvent.
Reason (R) Cryoscopic constant is a universal constant.

18 **Assertion** (A) Ethanol and acetone show positive deviation from Raoult's law.
Reason (R) Pure ethanol molecule show hydrogen bond and on adding acetone hydrogen bond between ethanol molecules breaks.

19 **Assertion** (A) Nitric acid and water form maximum boiling azeotrope. **CBSE SQP 2021**
Reason (R) Azeotropes are binary mixture having the same composition in liquid and vapour phase.

20 **Assertion** (A) The vapour pressure of 0.1M sugar solution is less than that of 0.1M potassium chloride solution.

Reason (R) Lowering of vapour pressure is directly proportional to the number of species present in the solution.

21 **Assertion** (A) NaCl in water and organic acids in benzene show abnormal molecular mass.

Reason (R) Abnormal molecular mass is obtained when the substance in the solution undergoes dissociation or association.

22 **Assertion** (A) Osmotic pressure is a colligative property. **CBSE 2021 (Term I)**

Reason (R) Osmotic pressure of a solution depends on the molar concentration of solute at any temperature *T*.

VERY SHORT ANSWER Type Questions

22 Why is osmotic pressure considered as a colligative property?

23 What possible value of '*i*' will it have, if solute molecules undergo association in solution?

24 A person suffering from high blood pressure should consume less common salt. Give reason.

25 What would be the value of van't Hoff factor for a dilute solution of Na_2SO_4 in water?

26 Give an example of solid solution in which the solute is a gas.

27 Why cannot we separate an azeotropic mixture by distillation?

28 *A* and *B* liquids on mixing produced a warm solution.Which type of deviation is this and why?

29 What is the sum of mole fractions of all the components in a three component system?

30 What do you mean by parts per million?

31 Express the quantity $\chi_i = \dfrac{n_i}{\Sigma n_i}$ in words.

32 Will the molality of a solution at 50°C be same, less or more than molarity at 25°C?

33 What is the molality of NH_3 in a solution containing 0.85g of NH_3 in 100 mL of a liquid of density 0.85g cm^{-3}?

34 What is the density of 3.60 M sulphuric acid, which is 29% H_2SO_4 by mass?

35 Define vapour pressure.

36 What type of liquids form ideal solutions?

37 What happens to vapour pressure of water if a table spoon of sugar is added to it?

38 How much urea should be dissolved in 50 g of water, so that its vapour pressure at room temperature is reduced by 25%?

39 Why the vapour pressure of the solution is found to be less than that of the solvent?

40 Give two basic differences between ideal and non-ideal solutions.

41 Between 2M glucose solution and 1M glucose solution, which one has a lower freezing point?

42 Sodium chloride solution freezes at lower temperature than water but boils at higher temperature than water. Why?

43 Are equimolar solutions of sodium chloride and urea isotonic? Give reason.

SHORT ANSWER Type I Questions

44 What type of liquids form non-ideal solutions?

45 An electrolyte *AB* is 50% ionised in aqueous solution. Calculate the freezing point of 1 molal aqueous solution.

46 Which out of molality, molarity and mole fraction of a solution will remain unchanged and why?

47 Why constant boiling mixtures behave like a single component when subjected to distillation?

48 Write four differences between solutions having positive deviation and solutions having negative deviations from Raoult's law.

49 Explain why the boiling point of a solvent is increased on dissolving a non-volatile solute into it?

50 What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions?

51 A solution prepared by dissolving 1.25 g of oil of winter green (methyl salicylate) in 99 g of benzene has a boiling point of 80.31°C and K_b for benzene is 2.53 K kg mol^{-1}. Find molar mass of the solute. Boiling point of benzene = 80°C.

52 Calculate the molality of K_2CO_3 solution which is formed by dissolving 2.5 g of it in 1 L of solution. Density of solution is 0.85 g mL^{-1}.

53 Distinguish between the terms molality and molarity. Under what conditions are the molarity and molality of a solution nearly the same?

54 Consider the solute-solvent interactions and arrange the following compounds in the order of increasing solubility in ethanol with suitable explanations.
NaCl, cycloheptane, H_2O, CH_3COCH_3

55 K_H value for Ar(*g*), $CO_2(g)$, HCHO(*g*) and $CH_4(g)$ are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively.
Arrange these gases in the order of their increasing solubility and giving suitable reason.

56 Why the solubility of Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) first increases upto 32.4°C and then decreases?

57 A solution obtained by mixing 300 g of 25% and 400 g of 40% solution by mass. Calculate the mass % of the resulting solution.

58 At 80°C, the vapour pressure of a pure liquid *A* is 520 mm of Hg and that of pure liquid *B* is 1000 mm of Hg. If a mixture of *A* and *B* boils at 80°C and 1 atm pressure, then what is the amount of *A* in the mixture?

59 A solution of chloroform and acetone is an example of maximum boiling azeotropes. Name and discuss the type of azeotrope.

60 How many grams of concentrated nitric acid solution should be used to prepare 250 mL of 2.0 M HNO_3? The concentrated acid is 70% HNO_3

61 Define the following terms:
(i) Isotonic solutions
(ii) Hypertonic solutions
(iii) Hypotonic solutions

62 A storage battery contains a solution of H_2SO_4, 38% by weight. At this concentration, van't Hoff factor is 2.50. At what temperature, will the battery contents freeze?

63 Four solutions of K_2SO_4 with the concentration 0.1 M, 0.01M, 0.001M and 0.0001M are available. For which concentration, there is maximum value of van't Hoff factor?

64 What is the value of van't Hoff factor for 0.1M ideal solution?

65 Calculate the freezing point of an aqueous solution containing 10.50 g of $MgBr_2$ in 200 g of water (molar mass of $MgBr_2$ = 184 g, K_f for water = 1.86 K kg mol^{-1}).

SHORT ANSWER Type II Questions

66 Discuss biological and industrial importance of osmosis.

67 Calculate the freezing point depression expected for 0.0711 m aqueous solution of Na_2SO_4. If this solution actually freezes at 0.320°C, what would be the value of van't Hoff factor? (K_f for water is 1.86°C mol^{-1})

68 A 5% solution (by mass) of cane sugar in water has a freezing point of 271 K. Calculate the freezing point of 5% (by mass) solution of glucose in water. The freezing point of pure water is 273.15 K. (Molar mass of cane sugar = 342 g mol^{-1} and molar mass of glucose = 180 g mol^{-1})

69 Explain with example the concept of minimum boiling azeotropes and maximum boiling azeotropes.

70 Write three differences between ideal and non-ideal solutions.

71 Explain, how the measurement of depression in freezing point can be used for the determination of molecular masses of non-volatile solutes?

72 (i) Why does the use of pressure cooker reduce cooking time?
(ii) How does van't Hoff factor helps in the determination of degree of association or dissociation of a solute in solution?

73 (i) Define molality in terms of elevation in boiling point.
(ii) Derive the relation between elevation in boiling point and the molecular mass of a non-volatile solute.

74 (i) If the membrane used for the determination of osmotic pressure is slightly torn, how will it influence the measured value of osmotic pressure?
(ii) The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to be 354.11 K. Calculate the molar mass of the solute.
(K_b for benzene is 2.53 K kg mol^{-1})

75 At what partial pressure, oxygen will have a solubility of 0.05 g L^{-1} in water at 293 K? [Henry's constant (K_H) for O_2 in water at 293 K is 34.86 k bar. Assume the density of the solution to be same as that of the solvent.]

76 State the law correlating the pressure of a gas and its solubility in a liquid. State an application of this law.

77 The solubility of pure nitrogen gas at 25°C and 1 atm is 6.8×10^{-4} mol L^{-1}. What is the concentration of nitrogen dissolved in water under atmospheric condition? The partial pressure of nitrogen gas in the atmosphere is 0.78 atm.

78 What mass of NaCl must be dissolved in 65.0 g of water to lower the freezing point of water by 7.50°C? The freezing point depression constant (K_f) for water is 1.86°C/m. Assume van't Hoff factor for NaCl is 1.87.
(Molar mass of NaCl = 58.5 g mol^{-1}).

79 (i) When dehydrated fruits and vegetables are placed in water, they slowly swell and return to original shape. Why? What is the effect of temperature on this process? Explain.
(ii) Prove that relative lowering in vapour pressure of a liquid on addition of non-volatile solute is a colligative property.

LONG ANSWER Type Questions

80 (i) Why does a solution of chloroform and acetone show negative deviation from Raoult's law?
(ii) State how the vapour pressure of a solvent is affected, when a non-volatile solute is dissolved in it?
(iii) A solution of glucose ($C_6H_{12}O_6$) in water is labelled as 10% by weight. What would be the molality of the solution? (Molar mass of glucose = 180 g mol^{-1})

81 (i) Two liquids X and Y boil at 100°C and 120°C respectively. Which of them has higher vapour pressure at 50°C and why?
(ii) Calculate the boiling point of a solution prepared by adding 15.00 g of NaCl to 250 g water.
(K_b for water = 0.512 K kg mol^{-1}; molar mass of NaCl = 58.44g)
(iii) Calculate the lowering of vapour pressure for 0.1 m aqueous solution of non-electrolyte at 75°C. ($\Delta H = 9.720$ K cal mol^{-1}, $p_2 = 742.96$ torr)

82 (i) Give the differences (any three) between ideal and non-ideal solutions.
(ii) Which of the following solutions will have the highest and lowest osmotic pressure? and why?
(a) Sugar in water
(b) Salt in water

83 (i) What is van't Hoff factor?
(ii) What possible values can it have if the solute molecules undergo dissociation?
(iii) An aqueous solution containing 12.48 g of barium chloride in 1.0 kg of water boils at 373.0832 K. Calculate the degree of dissociation of barium chloride.
(Given, K_b for $H_2O = 0.52$ K m^{-1}; molar mass of $BaCl_2 = 208.34$ g mol^{-1}).

ANSWERS

1 (c) **2** (a) **3** (d) **4** (b) **5** (b)

6 (b) When a non-volatile solid is added to a solvent then vapour pressure of solution is found to be lower than the vapour pressure of the pure solvent at the same temperature. It means, water boils below 100°C and freeze above 0°C.

7 (d) Colligative properties are proportional to the molar concentration of the solution, alongwith vapour pressure lowering, boiling point elevation freezing point elevate and osmotic pressure.
These are dependent only on the identity of the solvent and the concentration of the solute.

8 (a) Freezing point of solution is inversely proportional to concentration.
More concentration is lower will be freezing point. So, juice A has highest freezing point as it has lowest concentration.

9 (d) Colligative properties are vapour pressure lowering, boiling point elevation, depression in freezing point and osmotic pressure. Hence, all given options are colligative properties.

10 (a) The freezing point of the solution is always lower than that of pure solvent as the vapour pressure of the solvent decreases in the presence of non-volatile solute. Both (A) and (R) are true and (R) is the correct explanation of (A).

11 (b) Depression in freezing point $(\Delta T_f) = K_f \times m$

$$= \frac{K_f \times W_{\text{solute}} \times 1000}{W_{\text{solvent}} \times M_{\text{solute}}}$$

$$M_{solute} = \frac{K_f \times W_{solute} \times 1000}{\Delta T_f \times W_{solvent}}$$

Both (A) and (R) are true but (R) is not correct explanation of (A).

12 (c) Cryoscopic constant or molal freezing point depression constant (K_f) is defined as the depression in freezing point for 1 molal solution, i.e. a solution containing 1g mole of solute dissolved in 1000g of solvent.

Only (A) is true but (R) is false.

Or (a) Given, $W_{solute} = 5g$, $M_{solute} = 180$ g mol^{-1}

$W_{solvent} = 95$ g

Molality of glucose solution $= \frac{5}{180} \times \frac{1000}{95} = 0.2924$

$$\Delta T_f = K_f \times m$$

$$\Delta T_f = 13.962 \times 0.2924 = 4.08$$

Both (A) and (R) are true and (R) is correct explanation of (A).

13 (a) The constant K_f is not unit less because it has quantities like K, kg and mol.

Its unit is K kg mol^{-1}

Hence, both (A) and (R) are true and (R) is correct explanation of (A).

14 (b) Both (A) and (R) are true but (R) is not the correct explanation of (A). The correct explanation is that one molar aqueous solution has 1 mole in less than 1000 g of water. Hence, 1000 g of water will be associated with more than 1 mole while 1 molal has 1 mole in 1000 g of water.

15 (b) Aquatic species are more comfortable in cold water rather than in warm water because the solubility of gases decreases with increase of temperature.

16 (a) When the divers come towards the surface, pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. Hence, both (A) and (R) are correct and (R) is the correct explanation of (A).

17 (c) A is true but (R) is false.

The value of cryoscopic constant depends on the nature of the solvent. Hence, it is not a universal constant.

18 (a) Ethanol molecules show hydrogen bonding. On adding acetone, its molecules get in between the host molecule and break some of hydrogen bonds between them. Due to weakening of interaction, the mixture of ethanol and acetone shows the positive deviation from Raoult's law. Hence, both (A) and (R) are correct and (R) is the correct explanation of (A).

19 (b) Nitric acid and water form maximum boiling azeotropes. This solution shows large negative deviation from Raoult's law. Thus, both Assertion and Reason are correct and Reason is not the correct explanation of Assertion.

20 (d) Lowering of vapour pressure is directly proportional to the number of species present in solution. Sugar is a non-electrolyte however KCl is an electrolyte and dissociates in solution to give particles. Hence, there is greater lowering in vapour pressure in case of KCl. Hence, the vapour pressure of 0.1M sugar solution is more than that of 0.1 M potassium chloride solution. Thus, Assertion (A) is incorrect but Reason (R) is correct.

21 (a) Both (A) and (R) are true and (R) is the correct explanation of (A).

22 (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A). Osmotic pressure is a colligative property as it depends upon number of mole of solutes.

23 In association, observed molar mass being more than the normal, so i has a value less than one ($i < 1$).

24 People taking a lot of salt or salty food experience water retention in tissue cells and inter cellular spaces because of osmosis.

25 $Na_2SO_4 \rightleftharpoons 2\,Na^+ + SO_4^-$

26 Hydrogen in palladium.

27 Azeotropic mixtures have the same composition in liquid and vapour phase and boil at constant temperature, hence it is not possible to separate the components by fractional distillation.

28 On mixing A and B produced a warm solution, which means heat is evolved, i.e., exothermic. In case of negative deviation $\Delta H_{mix} < 0$, i.e. heat is evolved due to the formation of stronger bonds.

29 For a given solution, sum of all the mole fraction is unity, i.e., $x_1 + x_2 + x_3 + \ldots x_i = 1$

30 When a solute is present in trace quantities, the concentration is expressed in parts per million (ppm).

$$\text{ppm} = \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solutions}} \times 100$$

31 Mole fraction of a solution containing i number of components is the ratio of moles of i th component and the total moles of all the components.

32 **Hint** Molarity decreases with increase in temperature, hence, less at 50°C while molality remains constant.

33 Molality $= \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$ **[Ans** 0.597 m**]**

34 Molarity $= \frac{\text{Number of moles of solute}}{\text{Volume of solution (in litre)}}$ **[Ans** 1.22g /mL**]**

35 The pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature is called vapour pressure.

36 The solutions which obey Raoult's low over the entire range of concentration are known as ideal solution.

37 **Hint** Vapour pressure decreases, due non-volatile solute.

38 **Hint** Use the equation $\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{w_1 \times M_1}{w_2 \times M_2}$

[Ans 41.62 g**]**

39 In case of solid-liquid solution, the surface has both solute and solvent molecules; thereby the fraction of the surface covered by the solvent molecules gets reduced and thus decrease in vapour pressure occurs.

40 (i) Ideal solutions obey's Raoult law while non-ideal solution do not obey the Raoult's law

(ii) $\Delta_{mix}H$ and $\Delta_{mix}V = 0$ (ideal solution)

$\Delta_{mix}H$ and $\Delta_{mix}V \neq 0$ (non-ideal solution)

41 **Hint** Higher the concentration, lower is the freezing point.

42 Non-volatile solute lowers the freezing point of the solution and increases the boiling point of the solution.

43 Two solution having same osmotic pressure at a given temperature are called isotonic solutions.

$$\pi = iCRT \begin{pmatrix} i \text{ for NaCl} = 2 \\ i \text{ for urea} = 1 \end{pmatrix}$$

44 Refer to text on page 18.

45 [**Ans.** -2.79°C]

46 Refer to text on pages 3 and 4.

47 Refer to text on page 19.

48 Refer to text on page 19.

49 **Hint** Non-volatile solute decreases vapour pressure of a solution. Refer to text on page 26.

50 Refer to text on page 29.

51 [**Ans** 152.11×10^3 g mol^{-1}]

52 **Hint** Consider mass number as atomic number. [**Ans** 0.02 m]

53 Refer to text on page 4.

54 **Ans** $NaCl < H_2O < CH_3COCH_3 <$ Cyclopentane

55 Hint $Ar < CO_2 < CH_4 < HCHO$

56 **Hint** With rise in temperature, it loses water of crystallisation.

57 [**Ans** 6.65%]

58 [**Ans** Mole per cent of $A = 50\%$]

59 Refer to text on page 19.

60 [**Ans** 45 g]

61 Refer to text on page 30.

62 [**Ans** 29.06°C]

63 **Hint** Higher the concentration, lower is the value of van't Hoff factor.

64 **Hint** Consider no dissociation or association [**Ans** = 1]

65 [**Ans** $-0.146°$ C]

66 Refer to text on pages 29 and 30.

67 [**Ans** 0.397°C, 2.42]

68 [**Ans** 269.065 K]

69 Refer to text on page 19.

70 Refer to text on page 19.

71 Refer to text on page 28.

72 (i) **Hint** It does not let vapours escape

(ii) **Hint** van't Hoff factor (i) varies as

For association, $i < 1$ For dissociation, $i > 1$

73 (i) Refer to text on page 27.

(ii) Refer to text on page 27.

74 **Hint** Osmotic pressure will decrease [**Ans** 57.5 g mol^{-1}]

75 **Hint** $p = K_H \chi$ [**Ans** 1.834 bar]

76 Refer to text on page 11.

77 [**Ans** 5.3×10^{-4} m]

78 Refer to page 27. [**Ans** 28.678]

79 (i) Refer to text on page 29.

(ii) Refer to text on pages 25 and 26.

80 (i) Refer to text on page 19.

(ii) Refer to text on page 17.

(iii) [**Ans** 0.617 m]

81 (i) Refer to text on page 26.

[(ii) **Ans** 373.53 K, (iii) **Ans** 0.533]

82 Refer to text on pages 19 and 28-29.

83 (i), (ii) Refer to text on page 31. (iii) [**Ans** 83.33%]

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|02|

ELECTROCHEMISTRY

Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to carry out non-spontaneous chemical transformations. A large number of metals, sodium hydroxide, chlorine, fluorine and many other chemicals are produced by electrochemical methods.

Electrochemistry holds significance even in biological world. Studies have shown that, the transmission of sensory signals from cells to brain and *vice-versa* and communication between the cells involves electrochemical processes.

CHAPTER CHECKLIST

- Electrochemical Cells
- Conductivity of Electrolytic Solution and Its Measurements
- Electrolytic Cells and Electrolysis
- Electrochemical Cells in Action

|TOPIC 1| Electrochemical Cells

An electrochemical cell is a device in which chemical energy of the redox reaction is converted into electrical energy while electrolytic cell do the reverse.

$$\text{Chemical energy} \underset{\text{Electrolytic cell}}{\overset{\text{Electrochemical cell}}{\rightleftharpoons}} \text{Electrical energy}$$

Batteries and fuel cells convert chemical energy into electrical energy and are used in various instruments and devices. The reactions carried out electrochemically can be energy efficient and less polluting. Therefore, study of electrochemistry is important for creating new technologies that are eco-friendly.

Note

A chemical reaction in which electrons are lost by one substance and gained by another is called **redox reaction**. In redox reaction, transfer of electrons generate electric current.

The most common electrochemical cell is a galvanic cell or a voltaic cell. An improvement of galvanic cell is Daniell cell, which converts chemical energy liberated during redox reaction to electrical energy through following reaction,

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

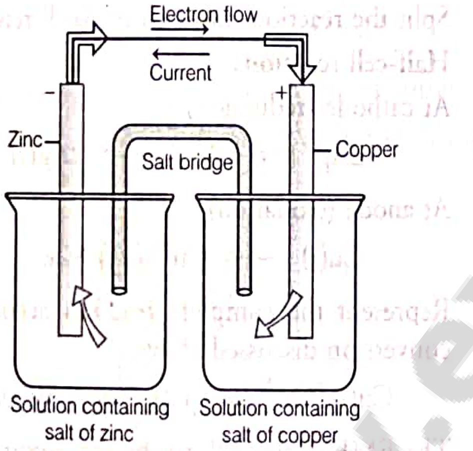
The above reaction generates an electric potential of 1.1 V, when concentration of Zn^{2+} and Cu^{2+} ions is unity ($1\ \text{mol dm}^{-3}$).

GALVANIC CELLS

Electrochemical cells which convert the chemical energy of a spontaneous redox reaction into electrical energy are called galvanic or voltaic cells. It is composed of two half-cells, each having different salt solutions, connected through an electric circuit (consisting of metal electrodes and conducting wire). Oxidation and reduction take place in different half-cells, which result in the development of potential difference between the two half-cells and hence, generates electricity. Here, the Gibbs energy of the spontaneous redox reaction is converted into electrical energy which may be used for running a motor or other electrical appliances like heater, geyser, fan, etc. An example of this type of device is Daniell cell.

Daniell Cell

It consists of zinc rod dipped in zinc sulphate solution and a copper rod in copper sulphate solution. These two solutions are connected by an electric circuit and a salt bridge as shown in the figure.



Daniell cell having Zn and Cu electrodes dipping in the solutions of their respective salts

Working

In this cell, an electrode is dipped into the solution of its own salt, this combination is called a half-cell or redox couple. In a half-cell, either a reduction or an oxidation reaction occurs. Oxidation occurs at **anode** whereas, reduction occurs at the **cathode**. The two half-cell reactions in a Daniell cell are:

(i) $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ (reduction half reaction)

(ii) $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ (oxidation half reaction)

The copper electrode may be called as the reduction half-cell and the zinc electrode, the oxidation half-cell.

The overall redox reaction occurs as

$$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

The two half-cells are connected by a metallic wire through a voltmeter and a switch, externally. The electrolytes of the two half-cells are connected internally through a salt bridge. Sometimes, both the electrodes are dipped in the same electrolyte solution and in such cases, we do not require a salt bridge.

> **Salt Bridge**
>
> It is a U-shaped glass tube containing electrolytes (KCl, KNO_3, NH_4Cl, etc.) mixed in some kind of gel (like gelatine or agar-agar). It plays an important role in working of electrochemical cell as it:
>
> - completes the circuit and
> - maintains the electrical neutrality of solutions in each of the respective half-cells.
>
> Salt bridge added in Daniell cell was as an improvement of original galvanic cell. In original cell, electricity flow stops after some time as positive charge accumulates at oxidation half-cell and negative at reduction half-cell which balance the redox free energy and hence, stops the redox reaction. But when salt bridge is present, it provides anions and cations to respective half-cells thus, maintaining the neutrality of both the half-cells.

An electrical potential energy of 1.1 V is generated from the Daniell cell, when the concentration of Zn^{2+} and Cu^{2+} ions is 1 mol dm^{-3}. If an external opposite potential is applied to the galvanic cell and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value of 1.1 V, the reaction stops altogether and no current flows through the cell.

Any further increase in the external potential, again starts the reaction but in opposite direction. It now functions as an **electrolytic cell**, a device for using electrical energy to carried out non-spontaneous chemical reactions. Hence, an electrochemical cell can behave like an electrolytic cell, when $E_{ext} > E_{cell}$.

Functioning of Daniell Cell in Presence of External Voltage

Following three cases are possible when E_{ext} is applied:

Case I **When the external potential is lower than 1.1V.** Under this condition, electrons flow from Zn rod to Cu rod. Hence, current flows from Cu to Zn. Zinc dissolves at anode and copper deposits at cathode.

Case II **When the external potential is equal to 1.1V.** Chemical reactions in the cell stop and there is no flow of electrons or current.

Case III **When the external potential is more than 1.1V.** The reactions get reversed and so, the polarity of the electrodes. This cell is then called an **electrolytic cell**. Now, electrons flow from Cu to Zn and current flows from Zn to Cu. Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

SOME IMPORTANT TERMS RELATED TO CELL

Electrode Potential

At each electrode-electrolyte interface, metal ions in the solution have a tendency to leave the electrolyte and deposit on the electrode, trying to make it positively charged. Similarly, at the metal electrode, the metal atoms lose electrons, making the electrode negatively charged and metal ions formed go to the electrolyte.

As a result of this, a separation of charge occurs at the electrode. Depending on the net charge at the equilibrium, the electrode may be positively or negatively charged with respect to the solution. In this way, a potential difference develops between the electrode and the electrolyte. This is called the **electrode potential.**

Standard Electrode Potential

The electrode potential under the conditions of unit concentration (1M) (i.e. the concentrations of all the species involved in a half-cell is unity) at 1atm pressure and 25°C (298 K) of all the species in the half-cell is called the **standard electrode potential**. According to the IUPAC convention, standard reduction potential of a cell is now called the standard electrode potential. The value of the oxidation potential of the same cell reaction will be the same with the reversed sign.

Cell Potential

In Daniell or galvanic cell, the anode is the negative electrode and the cathode is the positive electrode. So, there exists a potential difference between the two electrodes. The potential difference between the two half-cells is called the **cell potential** and is measured in volts . It is the difference between standard reduction potential of cathode and standard reduction potential of anode.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

When switch is in the on position, the flow of electrons is from negative electrode to the positive electrode and the direction of current flow is opposite to that of electron flow.

Electromotive Force (emf) of a Cell

It is the potential difference, when no current is drawn through the cell. It is measured in volts (V).

EMF = Reduction potential of cathode – Reduction potential of anode

It depends upon the following factors :

(i) nature of metal and its ions

(ii) concentrations of electrolytes used

(iii) temperature

Cell Representation

While representing the galvanic cell, the anode is written on the left and the cathode on the right. A vertical line separates the metal from the metal ion (electrolyte solution) and a double vertical line indicates a salt bridge connecting the two half-cells (two electrolytes). The state of the metal and the solution is written with the concentration of the electrolyte in parenthesis.

$$E_{cell} = E_{right\ (cathode)} - E_{left\ (anode)}$$

Let us consider an example to understand the concept.

Step I. Write the chemical reaction

Cell reaction

$$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

Step II. Split the reaction into two half-cell reactions.

Half-cell reactions

At cathode (reduction) :

$$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$$

At anode (oxidation)

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$

Step III. Represent the complete reaction according to the conversion discussed above.

$$Cu(s)\,|\,Cu^{2+}(aq)\,||\,Ag^+(aq)\,|\,Ag(s).$$

The EMF of the cell can be represented as

$$E_{cell} = E_{right} - E_{left}$$

For cell reaction;

$$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

$$E_{cell} = E_{Ag^+/Ag} - E_{Cu^{2+}/Cu}$$

EXAMPLE |1| (i) Formulate the electrochemical cell representing the reaction,

$$2Cr(s) + 3Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Fe\ (s)$$

(ii) Calculate E°_{cell}. **All India 2008 C**

[Given, $E^\circ_{Cr^{3+}/Cr} = -0.74$ V, $E^\circ_{Fe^{2+}/Fe} = -0.44$ V].

Sol. (i) Representation of the given cell,

$$Cr(s)\,|\,Cr^{3+}(aq)\,||\,Fe^{2+}(aq)\,|\,Fe(s)$$

(ii) $E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$

As, $E^\circ_{Cr^{3+}/Cr} = -0.74$ V ; $E^\circ_{Fe^{2+}/Fe} = -0.44$ V

$= -0.44 - (-0.74)$

$= -0.44 + 0.74 = 0.30$ V

Measurement of Electrode Potential

In order to compute the emf of a cell, we have to apply the relationship

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

However, individual cell emf cannot be measured. It is the potential difference between the two electrodes that is measurable in a circuit by a voltmeter.

Therefore, in order to measure the half-cell potential, the other half-cell in this set up has to be assigned an arbitrary value. This is done by assigning a potential of zero called a Standard Hydrogen Electrode (SHE).

Therefore, the potential difference recorded in the voltmeter in a cell circuit, one half-cell of which is the standard hydrogen electrode, is attributed to the other electrode.

The SHE is represented as:

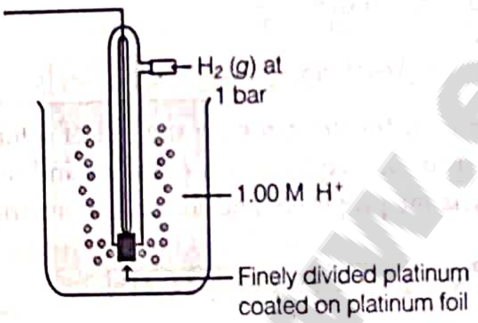
$$Pt(s)|H_2(g)|H^+(aq)$$

in which the reaction occurs as

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$$

and is assigned a zero potential at all temperatures.

The construction of the SHE is shown in the figure below:



Standard Hydrogen Electrode (SHE)

SHE consists of a platinum electrode coated with platinum black. The electrode is dipped in solution of 1M H^+ ions and pure H_2 gas is bubbled through it at 1 bar pressure. The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity.

At 298K, the emf is measured by combining the SHE of the anode with another half-cell of the cathode, resulting into the standard reduction potential of the other half-cell (cathode). In this manner, half-cell potentials are measured.

EMF of the cell $= E^\circ_{\text{cell}} = E^\circ_R - E^\circ_L$

As E°_L for SHE is zero, $E^\circ = E^\circ_R - 0 = E^\circ_R$

The superscript degree (°) indicates standard conditions.

Calculation of emf of the Cell

If we take the example of Daniell cell,

(i) The measured emf of the cell,

$$Pt(s)|H_2(g, 1\text{bar})|H^+(aq, 1M)||Cu^{2+}(aq, 1M)|Cu$$

and the value for the standard electrode potential of the half-cell reaction,

$Cu^{2+}(aq, 1M) + 2e^- \longrightarrow Cu(s)$ is equal to 0.34 V.

(ii) Similarly, the measured emf of the cell,

$$Pt(s)|H_2(g, 1\text{bar})|H^+(aq, 1M)||Zn^{2+}(aq, 1M)|Zn$$

and the value for the standard electrode potential of the half-cell reaction,

$Zn^{2+}(aq, 1M) + 2e^- \longrightarrow Zn(s)$ is equal to -0.76V.

(iii) The positive value of the standard electrode potential in the first case indicates that Cu^{2+} ions get reduced more easily than H^+ ions. In other words, we can say that hydrogen gas can reduce copper ion under the standard conditions. Thus, Cu does not dissolve in HCl. In nitric acid, copper is oxidised by nitrate ion and not by hydrogen ion.

(iv) The negative value of the standard electrode potential in the second case indicates that H^+ ions can oxidise zinc. In other words, we can say that zinc ions can reduce hydrogen ions.

(v) Taking sign convention, the half-cell reactions for the Daniell cell can be written as:

$$Zn(s) \longrightarrow Zn^{2+}(aq, 1M) + 2e^-$$

(at left electrode)

$$Cu^{2+}(aq, 1M) + 2e^- \longrightarrow Cu(s)$$

(at right electrode)

The overall cell reaction can be written as:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

EMF of the cell $= E^\circ_{\text{cell}} = E^\circ_R - E^\circ_L$

$= 0.34$ V $- (-0.76)$V $= 1.10$V

Note

Some metals like platinum or gold are used as inert electrodes. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for the conduction of electrons, e.g.

Pt is used in hydrogen electrode : $Pt(s)|H_2(g)|H^+(aq)$

with half-cell reaction, $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$

Bromine electrode : $Pt(s)|Br_2(aq)|Br^-(aq)$

with half-cell reaction, $\frac{1}{2}Br_2(aq) + e^- \longrightarrow Br^-(aq)$

ELECTROCHEMICAL SERIES AND ITS APPLICATIONS

The arrangement of various standard half-cells in the order of their decreasing values of standard reduction potentials is called electrochemical series.

Standard electrode potentials at 298K
(Electrochemical series)

Increasing strength of oxidising agent (upwards) — Increasing strength of reducing agent (downwards)

Reaction (oxidised form + ne^- $\longrightarrow$ reduced form)		E°/V
$F_2(g) + 2e^-$	$\longrightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\longrightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^-$	$\longrightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^-$	$\longrightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^-$	$\longrightarrow Au(s)$	1.40
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\longrightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^-$	$\longrightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^-$	$\longrightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^-$	$\longrightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^-$	$\longrightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^-$	$\longrightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\longrightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\longrightarrow H_2O_2$	0.68
$I_2 + 2e^-$	$\longrightarrow 2I^-$	0.54
$Cu^+ + e^-$	$\longrightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\longrightarrow Cu(s)$	0.34
$AgCl(s) + e^-$	$\longrightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^-$	$\longrightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^-$	$\longrightarrow H_2(g)$	0.00
$Pb^{2+} + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Sn^{2+} + 2e^-$	$\longrightarrow Sn(s)$	−0.14
$Ni^{2+} + 2e^-$	$\longrightarrow Ni(s)$	−0.25
$Fe^{2+} + 2e^-$	$\longrightarrow Fe(s)$	−0.44
$Cr^{3+} + 3e^-$	$\longrightarrow Cr(s)$	−0.74
$Zn^{2+} + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+} + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+} + 2e^-$	$\longrightarrow Mg(s)$	−2.36
$Na^+ + e^-$	$\longrightarrow Na(s)$	−2.71
$Ca^{2+} + 2e^-$	$\longrightarrow Ca(s)$	−2.87
$K^+ + e^-$	$\longrightarrow K(s)$	−2.93
$Li^+ + e^-$	$\longrightarrow Li(s)$	−3.05

Note (i) Negative E° means that the redox couple is stronger reducing agent than H^+/H_2, e.g. Zn (−0.76).

(ii) Positive E° means that the redox couple is a weaker reducing agent than H^+/H_2, e.g. Ag (+ 0.80).

Standard half-cell potential values give various of information. If the standard electrode potential of an electrode is greater than zero, then its reduced form is more stable as compared to hydrogen gas. Similarly, if standard electrode potential is less than zero (negative value), hydrogen gas is more stable than the reduced form of the species.

Standard reduction potentials of half-cells are arranged from the highest (positive) value to the lowest (negative) value in a table. More negative the emf value, stronger is the reducing agent. The more positive the emf value, the weaker is the reducing agent as it is compared to H^+/H_2.

As one goes from top to bottom in the table in which electrochemical half-cells are arranged in the order of highest reduction potential to the lowest, the reducing power increases, whereas from the bottom of the table to the top, the oxidising power increases.

In other words, we can say that, from top to bottom in the table, the standard electrode potential decreases and with this, decreases the oxidising power of the species on the left and increases the reducing power of the species on the right hand side of the reaction. Electrochemical series also helps to predict the feasibility of a redox reaction, thermal stability of metal oxides and spontaneity of an electrochemical cell by choosing the half-cells with appropriate E° values.

Uses of Electrochemical Cells

These are used for determining the pH of solutions, solubility product, equilibrium constant and other thermodynamic properties and for potentiometric titrations.

NERNST EQUATION

The equation which gives the relation between electrode potential, temperature and concentration of metal ions is called Nernst equation.

Nernst Equation for Electrode Potential

The standard potentials are always measured under standard conditions, i.e. when the pressure of a gas is 1 atm, concentration of ions is 1 mol dm^{-3} and the temperature is 298 K. However, practically standard conditions are hardly achieved or used. According to Nernst, the electrode reaction is :

$$M^{n+}(aq) + ne^- \longrightarrow M(s)$$

The electrode potential measured against standard hydrogen electrode, can be written as

$$\boxed{E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}}$$

This is known as the **Nernst equation.**
For pure solids, $[M] = 1$

$$E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]} \quad \ldots(i)$$

Here, $E^\circ_{(M^{n+}/M)}$ is the standard reduction potential of the electrode, R is the universal gas constant having value 8.314 $\text{JK}^{-1}\text{mol}^{-1}$, n is the number of electrons involved in the reaction, T is the temperature in K, $[M^{n+}]$ is the concentration of the metal ion M^{n+}, and F is the Faraday constant whose value is 96500 C mol^{-1} (approx.).

Using logarithm to the base 10 value, Eq. (i) becomes,

$$E = E^\circ - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}]}$$

At $T = 298$ K, and putting values of all constants, we get,

$$\boxed{E = E^\circ - \frac{0.059}{n}\log\frac{1}{[M^{n+}]}}$$

Nernst Equation for emf of a Cell

For the cathode of Daniell cell, the emf is

$$E_{(Cu^{2+}/Cu)} = E^\circ_{(Cu^{2+}/Cu)} - \frac{RT}{2F}\ln\frac{1}{[Cu^{2+}(aq)]}$$

For the anode of Daniell cell, the emf is

$$E_{(Zn^{2+}/Zn)} = E^\circ_{(Zn^{2+}/Zn)} - \frac{RT}{2F}\ln\frac{1}{[Zn^{2+}(aq)]}$$

The cell potential of the Daniell cell is given by

$$E_{cell} = E_{(Cu^{2+}/Cu)} - E_{(Zn^{2+}/Zn)}$$

$$= E^\circ_{(Cu^{2+}/Cu)} - \frac{RT}{2F}\ln\frac{1}{[Cu^{2+}(aq)]} - E^\circ_{(Zn^{2+}/Zn)} + \frac{RT}{2F}\ln\frac{1}{[Zn^{2+}(aq)]}$$

$$E_{cell} = E^\circ_{(Cu^{2+}/Cu)} - E^\circ_{(Zn^{2+}/Zn)} - \frac{RT}{2F}\left[\ln\frac{1}{[Cu^{2+}(aq)]} - \ln\frac{1}{[Zn^{2+}(aq)]}\right]$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{2F}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

At T = 298 K,

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}}$$

According to the above equation,

- E_{cell} is directly dependent upon concentration of Cu^{2+} and inversely dependent upon the concentration of Zn^{2+} ions.
- E_{cell} decreases as temperature decreases and number of electrons involved in the reaction increases.

For a general electrochemical reaction of the type,

$$aA + bB \xrightarrow{ne^-} cC + dD$$

The Nernst equation can be written as:

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q}$$

$$\Rightarrow \quad E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

At $T = 298$ K,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

EXAMPLE |2| Calculate emf of the following cell at 25°C.
$Fe|Fe^{2+}(0.001M)||H^+(0.01M)|H_2(g)\ (1bar)|Pt(s)$
$E^\circ_{(Fe^{2+}/Fe)} = -0.44$ V; $E^\circ_{(H^+/H_2)} = 0.00$V **Delhi 2015**

Sol. For the given cell representation, the cell reaction will be

$$Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)$$

The standard emf of the cell will be,

$$E^\circ_{cell} = E^\circ_{H^+/H_2} - E^\circ_{Fe^{2+}/Fe},\quad E^\circ_{cell} = 0 - (-0.44) = 0.44\text{ V}$$

The Nernst equation for the cell reaction at 25°C,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Fe^{2+}]}{[H^+]^2}$$

$$= 0.44 - \frac{0.0591}{2}\log\frac{[0.001]}{[0.01]^2}$$

$$= 0.44 - 0.02955\ (\log 10)$$

$$= 0.44 - 0.02955\ (1) \qquad [\because \log 10 = 1]$$

$$= 0.41045\text{ V} = 0.41\text{ V}$$

Equilibrium Constant from Nernst Equation

In Daniell cell, the following reaction takes place

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

As the time passes, the reaction proceeds. The concentration of Zn^{2+} keeps on increasing and the concentration of Cu^{2+} keeps on decreasing. At the same time, voltage of the cell on the voltmeter keeps on decreasing. After sometime, there is no change in the concentration of Cu^{2+} and Zn^{2+} ions and at that time, voltmeter gives zero reading.

At equilibrium, when there is no current in the circuit, a Daniell cell shows zero potential in the voltmeter.

$$\text{Therefore, } E_{cell} = 0 = E^\circ_{cell} - \frac{2.303\,RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\text{or} \quad E^\circ_{cell} = \frac{2.303\,RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

At equilibrium, for the reaction

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_C$$

Therefore, at 298 K, the above equation can be written as:

$$E^\circ_{cell} = \frac{0.0591}{2}\log K_C = 1.1\text{ V}$$

which gives the K_C value as:

$$\log K_C = \frac{(1.1\text{ V}\times 2)}{0.059\text{ V}} = 37.288$$

$$K_C = 2\times 10^{37} \text{ at } 298\text{ K}$$

Such a high value of K_C shows that the reaction has proceeded almost to the completion before attainment of equilibrium condition.

Hence, the value of K_C determines the extent of cell reaction. In general, at equilibrium

$$\boxed{E^\circ_{cell} = \frac{2.303\,RT}{nF}\log K_C}$$

Thus, the above equation gives a relationship between equilibrium constant of the reaction and standard potential of the cell in which that reaction takes place. Thus, equilibrium constant of the reaction is difficult to measure otherwise, can be calculated from the corresponding E° value of the cell.

Concentration Cells

Two electrodes of the same metal dipped separately into two solutions of the same electrolyte having different concentrations and the solutions are connected through salt bridge, such cells are known as concentration cells, e.g. copper ion concentration cell.

$$Cu \mid Cu^{2+}(C_1) \parallel Cu^{2+}(C_2) \mid Cu$$

$$E_{cell} = \frac{0.0591}{n}\log\frac{C_2}{C_1}, \text{ where } C_2 > C_1 \text{ and } E^\circ_{cell} = 0$$

The electrode placed in high concentration electrolyte acts as cathode and that placed in low concentration electrolyte acts as anode.

EXAMPLE |3| Calculate the equilibrium constant for the reaction.

$$Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$$

[Given, $E^\circ_{Cd^{2+}/Cd} = -0.40\text{V}$, $E^\circ_{Fe^{2+}/Fe} = -0.44\text{ V}$]

Delhi 2009; Foreign 2009

(i) First, find E°_{cell} by using formula,

$$E^\circ_{cell} = E^\circ_{right} - E^\circ_{left} \text{ or } E^\circ_{cathode} - E^\circ_{anode}$$

(ii) Find $\log K_C$ by using formula,

$$E^\circ_{cell} = \frac{0.0591}{n}\log K_C$$

(iii) Find K_C using antilog table.

Sol. $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$$= -0.40 - (-0.44) = -0.40 + 0.44 = 0.04\text{ V}$$

$$E^\circ_{cell} = \frac{0.059}{n}\log K_C$$

$$E^\circ_{cell} = \frac{0.059}{2}\log K_C = 0.04$$

$$\text{or} \quad \log K_C = \frac{2\times 0.04}{0.059} = 1.356$$

$$K_C = \text{antilog}\,1.356 = 22.70$$

Electrochemical Cell and Gibbs Energy of the Reaction

When a cell reaction takes place, electrical energy is produced. Thus, electrical work done by the cell results in corresponding decrease in the free energy of the cell. Electrical work done in one second is equal to the electrical potential multiplied by total charge passed.

To obtain maximum work from a galvanic cell, charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to the decrease in its Gibbs energy. Let nF is the amount of charge passed, E is the emf of the cell and $\Delta_r G$ is the Gibbs energy of the reaction, then

$$\Delta_r G = -nFE_{cell}$$

Under standard conditions (i.e. when molar concentration of all reacting species is unity at 298 K), the emf of a cell is related to the Gibbs free energy as:

$$\Delta_r G^\circ = -nFE^\circ_{cell}$$

where, n is the number of electrons involved in the reaction and F is the Faraday's constant.

The relation between cell potential (E°_{cell}), free energy (ΔG°) and equilibrium constant is given by

$$\text{or} \quad \boxed{\Delta_r G^\circ = -2.303\,RT\log K_C}$$

$$\text{as } \Delta G^\circ = nFE^\circ_{cell} \text{ and } E^\circ_{cell} = \frac{2.303RT}{nF}\log K_C$$

E_{cell} is an intensive property but ΔG is an extensive thermodynamic property whose value depends on n.

Thus, if we write the reaction,

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s),$$
$$\Delta_r G = -2FE_{cell}$$

But when we write the reaction,

$$2Zn(s) + 2Cu^{2+}(aq) \longrightarrow 2Zn^{2+}(aq) + 2Cu(s),$$
$$\Delta_r G = -4FE_{cell}$$

If the concentration of all the reacting species is unity, then $E_{cell} = E^\circ_{cell}$

and we have $\Delta_r G^\circ = -nFE^\circ_{cell}$

E°_{cell} measurement can give us the value of thermodynamic quantity, $\Delta_r G^\circ$, standard Gibbs energy of the reaction which latter help in the calculation of equilibrium constant by the equation, $\Delta_r G^\circ = -RT \ln K$.

> **IMPORTANT POINT**
>
> At the stage of chemical equilibrium in the cell, $E_{cell} = 0$
>
> $\Delta_r G = -nFE_{cell} = -nF \times 0 = 0$
>
> The reaction is feasible only, when
>
> E_{cell} = positive or $\Delta_r G$ = negative.

EXAMPLE |4| The standard electrode potential (E°) for Daniell cell is +1.1 V. Calculate, the ΔG° for the reaction.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

$(1\ F = 96500\ C\ mol^{-1})$ **All India 2013**

Sol. $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

$E^\circ = +1.1\ V, \Delta G^\circ = ?$

$1F = 96500\ C\ mol^{-1}, n = 2$

$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.1$

$= -212300\ J\ mol^{-1}$

EXAMPLE |5| Calculate the cell emf and $\Delta_r G^\circ$ for the cell reaction at 25° C.

$$Zn(s) \mid Zn^{2+}(0.1M) \| Cd^{2+}(0.01M) \mid Cd(s)$$

[Given, $E^\circ_{Zn^{2+}/Zn} = -0.763$ V,
$E^\circ_{Cd^{2+}/Cd} = -0.403$ V
$1F = 96500\ C\ mol^{-1}$,
$R = 8.314\ JK^{-1}mol^{-1}$] **All India 2009C**

> Find $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ then, $\Delta_r G^\circ$ by using formula, $\Delta_r G^\circ = -nFE^\circ_{cell}$

Sol. $E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$

$= -0.403 - (-0.763) = 0.36$ V

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[Zn^{2+}(aq)]}{[Cd^{2+}(aq)]}$$

$$E_{cell} = 0.36 - \frac{0.059}{2} \log \frac{0.1}{0.01} \quad [n = 2]$$

$E_{cell} = 0.36 - 0.0295 \log 10$

$= 0.36 - 0.0295 \times 1 = 0.3305$ V

$\Delta_r G^\circ = -nFE^\circ_{cell} = -2 \times 96500 \times 0.36$

$= -69480\ J\ mol^{-1} = -69.48\ kJ\ mol^{-1}$

TOPIC PRACTICE 1

OBJECTIVE Type Questions

1. $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

   The above redox reaction is used in
   (a) Galvanic cell (b) Daniell cell
   (c) Voltaic cell (d) All of these

2. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called......... **NCERT Exemplar**
   (a) cell potential (b) cell emf
   (c) potential difference (d) cell voltage

3. Electrode potential of any electrode depends on
   (a) nature of metal (b) temperature of solution
   (c) molarity of solution (d) All of these

4. E°_{cell} of the reaction is

   $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$;
   [If $E^\circ_{Zn^{2+}/Zn} = -0.76$, $E^\circ_{Cu^{2+}/Cu} = 0.34$ V]
   (a) 0.34V (b) −0.76 V (c) +1.10 V (d) −1.10 V

5. Using the data given below find out the strongest reducing agent. **NCERT Exemplar**

   $E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33V$; $E^\circ_{Cl_2/Cl^-} = 1.36V$
   $E^\circ_{MnO_4^-/Mn^{2+}} = 1.51V$; $E^\circ_{Cr^{3+}/Cr} = -0.74V$
   (a) Cl^- (b) Cr (c) Cr^{3+} (d) Mn^{2+}

6. The standard reducing electrode potentials of three metallic cations, *viz* x, y and z are +0.52, −3.03 and −1.18 V respectively. The order of reducing capability of the related metals is
   (a) $y > z > x$ (b) $x > y > z$ (c) $z > y > x$ (d) $z > x > y$

7. In an electrochemical process, a salt bridge is used **Delhi 2020**
(a) as a reducing agent
(b) as an oxidising agent
(c) to complete the circuit so that current can flow
(d) None of the above

8. For the reaction, $M^{n+}(aq)+ne^- \longrightarrow M(s)$, select the best suitable representation of Nernst equation, when the solid M is taken.
(a) $E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$
(b) $E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$
(c) $E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M^{n+}]}{[M]}$
(d) $E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{RT}{nF} \ln [M^{n+}]$

9. Calculate the equilibrium constant for the reaction,
$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$
[Given, $E^\circ_{cell} = 1.1$ V]
(a) 2×10^{32} (b) 2×10^{34} (c) 2×10^{37} (d) 2×10^{39}

10. The electrode potential is known as standard electrode potential
(a) when it is reduction potential (according to IUPAC)
(b) when concentrations of all the species involved is unity
(c) when it is oxidation potential (according to IUPAC)
(d) Both (a) and (b)

VERY SHORT ANSWER Type Questions

11. Represent the galvanic cell in which the reaction, $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$ takes place. **Delhi 2013 C**

12. Arrange the following metals in the order in which they displace each other from the solution of their salts.
Al, Cu, Fe, Mg and Zn **NCERT**

13. If a reaction has an equilibrium constant $K<1$, then E° is positive or negative? What is the value of K, when $E^\circ = 0$ V ?

14. Under what condition,
$E_{cell} = 0$ or $\Delta G = 0$? **NCERT Exemplar**

SHORT ANSWER Type I Questions

15. Can you store copper sulphate solution in a zinc pot? **NCERT Intext**

16. Given the standard electrode potentials,
$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V
$Hg^{2+}/Hg = 0.79$ V, $Mg^{2+}/Mg = -2.37$ V,
$Cr^{3+}/Cr = -0.74$ V
Arrange these metals in their increasing order of reducing power. **NCERT**

17. Following reactions can occur at cathode during the electrolysis of aqueous silver nitrate solution using Pt electrodes:
$$Ag^+(aq) + e^- \longrightarrow Ag(s);\ E^\circ = 0.80 \text{ V}$$
$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g);\ E^\circ = 0.00 \text{ V}$$
On the basis of their standard electrode potential values, which reaction is feasible at cathode and why? **All India 2017 C**

18. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10. **NCERT Intext**

19. Calculate the emf of the cell in which the following reaction takes place.
$Ni(s) + 2Ag^+(0.002\ M) \rightarrow Ni^{2+}(0.160\ M) + 2Ag(s)$
Given that, $E^\circ_{cell} = 1.05$ V **NCERT Intext**

20. Use the data to answer the following and also justify giving reason : **All India 2019**

	Cr	Mn	Fe	Co
$E^0_{M^{2+}/M}$	−0.91	−1.18	−0.44	−0.28
$E^0_{M^{3+}/M^{2+}}$	−0.41	+1.57	+0.77	+1.97

(a) Which is a stronger reducing agent in aqueous medium, Cr^{2+} or Fe^{2+} and why?
(b) Which is the most stable ion in +2 oxidation and why?

SHORT ANSWER Type II Questions

21. How would you determine the standard electrode potential of the system Mg^{2+}/Mg? **NCERT Intext**

22. Write the Nernst equation and emf of the following cell at 298 K.
(i) $Mg(s) \mid Mg^{2+}(0.001\ M) \parallel Cu^{2+}(0.0001\ M) \mid Cu(s)$
(ii) $Fe(s) \mid Fe^{2+}(0.001\ M) \parallel H^+(1\ M) \mid H_2(g)(1\ \text{bar}) \mid Pt(s)$
Given that, $E^\circ_{Mg^{2+}/Mg} = -2.36$ V, $E^\circ_{Cu^{2+}/Cu} = 0.34$ V, $E^\circ_{Fe^{2+}/Fe} = -0.44$ V **Delhi 2013; NCERT**

23. Write the cell reaction and Nernst equation for the cell reaction in the Daniell cell. How will the E_{cell} be affected when concentration of Zn^{2+} ions is increased? **NCERT Exemplar**

24. Calculate the emf of the following cell at 25°C
$Ag(s)|\,Ag^{+}(10^{-3}M)||\,Cu^{2+}(10^{-1}M)|\,Cu(s)$
Given, E°_{cell} = +0.46 V and $\log 10^{n} = n$.
All India 2013

25. Calculate the emf of the following cell at 298 K.
$$2Cr(s) + 3Fe^{2+}(0.1M) \longrightarrow 2Cr^{3+}(0.01M) + 3Fe(s)$$
Given, $E^{\circ}_{(Cr^{3+}/Cr)} = -0.74$ V, $E^{\circ}_{(Fe^{2+}/Fe)} = -0.44$ V
Delhi 2016

26. Calculate $\Delta_r G^{\circ}$ and $\log K_c$ for the following reaction :
$$Cd^{2+}(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Cd(s)$$
Given : $E^{0}_{Cd^{2+}/Cd} = -0.403$ V
$E^{0}_{Zn^{2+}/Zn} = -0.763$ V
All India 2019

27. In the button cell, widely used in watches and other devices, the following reaction takes place
$$Zn(s) + Ag_2O(s) + H_2O(l) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^{-}(aq)$$
Determine E° and ΔG° for the reaction.
(Given, $E^{\circ}_{Ag^{+}/Ag} = +0.80$ V, $E^{\circ}_{Zn^{2+}/Zn} = -0.76$ V)
NCERT; Delhi 2012

28. Calculate $\Delta_r G^{\circ}$ and $\log K_C$ for the following reaction at 298 K.
$$2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd(s)$$
[Given: $E^{\circ}_{cell} = +0.34$ V, $F = 96500$ C mol^{-1}]
All India 2017 C

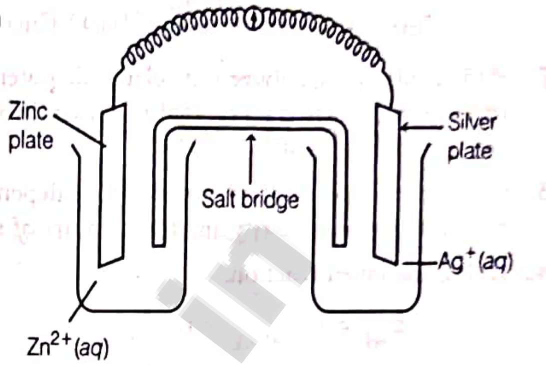
29. Calculate the standard cell potential of a galvanic cell in which the following reaction takes place
$$2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd(s)$$
Calculate $\Delta_r G^{\circ}$ and equilibrium constant, K of the above reaction at 25°C.
[Given, $E^{\circ}_{Cr^{3+}/Cr} = -0.74$ V, $E^{\circ}_{Cd^{2+}/Cd} = -0.40$ V, 1 F = 96500 C mol^{-1}]

30. The cell in which the following reaction occurs,
$$2Fe^{3+}(aq) + 2I^{-}(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$$
has $E^{\circ}_{cell} = 0.236$ V at 298 K, calculate the standard Gibbs energy and the equilibrium constant of the cell reaction. **NCERT Intext**

LONG ANSWER Type Questions

31. (a) When a bright silver object is placed in the solution of gold chloride, it acquires a golden tinge but nothing happens when it is placed in a solution of copper chloride.
Explain this behaviour of silver.
[Given: $E^{\circ}_{Cu^{2+}/Cu} = +0.34$; $E^{\circ}_{Ag^{+}/Ag} = +0.80$ V, $E^{\circ}_{Au^{3+}/Au} = +1.40$ V]

(b)



Consider the figure given above and answer the following questions:
(i) What is the direction of flow of electrons?
(ii) Which one is anode and which one is cathode?
(iii) What will happen if the salt bridge is removed?
(iv) How will concentration of Zn^{2+} and Ag^{+} ions be affected when the cell functions?
(v) How will concentration of these ions be affected when the cell becomes dead?
Delhi 2017 C

32. Depict the galvanic cell in which the reaction
$$Zn(s) + 2Ag^{+}(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$
takes place.
Further show
(i) which of the electrode is negatively charged?
(ii) the carriers of the current in the cell.
(iii) an individual reaction at each electrode.
NCERT

33. Using the standard electrode potentials, predict if the reaction between the following is feasible.
(i) $Fe^{3+}(aq)$ and $I^{-}(aq)$ (ii) $Ag^{+}(aq)$ and $Cu(s)$
(iii) $Fe^{3+}(aq)$ and $Br^{-}(aq)$ (iv) $Ag(s)$ and $Fe^{3+}(aq)$
(v) $Br_2(aq)$ and $Fe^{2+}(aq)$
Given standard electrode potentials,
$E^{\circ}_{1/2 I_2, I^{-}} = 0.541$ V, $E^{\circ}_{Cu^{2+}, Cu} = 0.34$ V,
$E^{\circ}_{1/2 Br_2, Br^{-}} = 1.09$ V, $E^{\circ}_{Ag^{+}, Ag} = 0.80$ V
$E^{\circ}_{Fe^{3+}, Fe^{2+}} = 0.77$ V
NCERT

34. Calculate the standard cell potentials of galvanic cell in which the following reactions takes place
(i) $2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd$
(ii) $Fe^{2+}(aq) + Ag^{+}(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$
Calculate the $\Delta_r G^{\circ}$ and equilibrium constant for these reactions.
NCERT

HINTS AND EXPLANATIONS

1. (*d*) Galvanic cells are also known as voltaic cells, e.g. Daniell cell. The reaction occuring in this cell is

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

2. (*b*) The difference between the electrode potential of two electrodes when no current is drawn through the cell is called cell emf.

3. (*d*) Electrode potential of any electrode depends on nature of metal, molarity and temperature of solution.

4. (*c*) For the given reaction,

$$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn}$$
$$= 0.34 - (-0.76) = +1.10\ V$$

5. (*b*) Here, out of given four options standard reduction potential of chromium has highest negative value hence most powerful reducing agent is chromium.

6. (*a*) More (–)ve be the value of standard reduction potential, stronger be the reducing strength (ability). Hence, correct order is $y > z > x$.

7. (*c*) In an electrochemical process, a salt-bridge is used.
   (i) To complete the circuit, so that current can flow.
   (ii) To maintain the electrical neutrality of the solution in the half cells.

8. (*b*) Electrode potential of an electrode is measured with respect to standard hydrogen electrode by the expression

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

but concentration of solid M is taken as unity

So, $$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]}$$

9. (*c*) $$E^\circ_{cell} = \frac{0.059}{2}\log K_C$$

$\therefore$ $$\log K_C = \frac{1.1 \times 2}{0.059} = 37.288$$

Thus, $$K_C = 2 \times 10^{37} \text{ at } 298\ K$$

10. (*d*) According to IUPAC convention when it is reduction potential and when concentrations of all the species involved is unity, then electrode potential is known as standard electrode potential.

11. The galvanic cell for the given reaction is

$$\underset{\text{Anode}}{Zn \mid Zn^{2+}} \underset{\text{Salt bridge}}{\parallel} \underset{\text{Cathode}}{Cu^{2+} \mid Cu}$$

12. The order in which the metals displace each other from their salts solution is

Mg, Al, Zn, Fe, Cu

13. $$E^\circ = \frac{0.0591}{n}\log K$$

If $K < 1$ (say 0.01), then

$$E^\circ = \frac{0.0591}{n}\log 0.01 = \frac{-2 \times 0.0591}{n}$$

E° is thus negative.

If $E^\circ = 0V$, then $K = 1$

14. At the stage of chemical equilibrium in the cell.

15. No, zinc pot cannot store copper sulphate solution because the standard electrode potential (E°) value of zinc (–0.76 V) is less than that of copper (–0.34 V). So, zinc is stronger reducing agent than copper.

16. The lower the reduction potential, the higher is the reducing power.

$$Ag < Hg < Cr < Mg < K$$

17. $Ag^+(aq) + e^- \longrightarrow Ag(s);\ E^\circ = 0.80\ V.$

Reaction is feasible at cathode because it has higher reduction potential.

18. For hydrogen electrode, $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

Applying Nernst equation,

$$E_{(H^+/1/2H_2)} = E^\circ_{(H^+/1/2H_2)} - \frac{0.0591}{n}\log\frac{1}{[H^+]}$$
$$= 0 - \frac{0.0591}{1}\log\frac{1}{(10^{-10})}$$
$$(\because pH = 10,\ [H^+] = 10^{-10}M)$$
$$= 0 - \frac{0.0591}{1} \times (10 \log 10) = -0.591\ V$$

Thus, $E_{(H^+/1/2H_2)} = -0.591\ V$

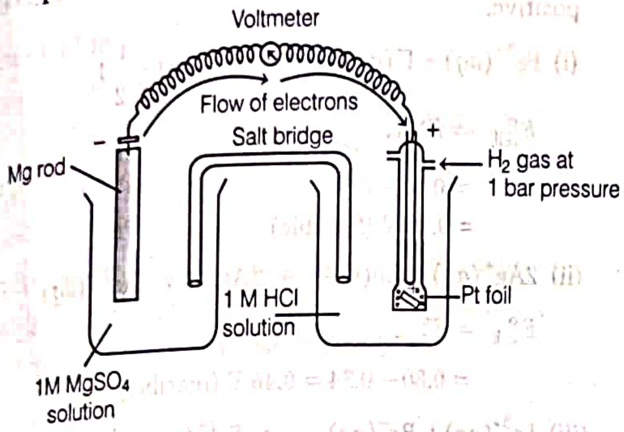
19. From the given cell reaction and Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$$
$$= 1.05\ V - \frac{0.0591}{2}\log\frac{(0.160)}{(0.002)^2}$$
$$= 1.05 - \frac{0.0591}{2}\log(4 \times 10^4)$$
$$= 1.05 - \frac{0.0591}{2}(4.6021)$$
$$= 1.05 - 0.135 = 0.915\ V$$
$$E_{cell} = 0.915\ V$$

20. (a) $\because$ Reactivity series is made on the basis of standard reduction potential (E°) and E° for Cr is more (-)ve than that of Fe. Thus, Fe get reduced and Cr get oxidised, in other words Cr is a stronger reducing agent.

(b) Among the given ions, the ion with more (-) ve value of E° (red.) will loose the electron more easily, thus is more stable in (+) 2 oxidation state. Hence Mn in (+) 2 oxidation state is the most stable species.

21. $E°$ value of Mg^{2+}/Mg electrode is determined by setting up an electrochemical cell.



The cell may be represented as:

$Mg\,|\,Mg^{2+}(1\,M)|\,H^+(1M)|\,H_2(1\text{ bar}), Pt\,(s)$

The reading given by voltmeter, gives $E°_{cell}$

$$E°_{cell} = E°_{(H^+/\frac{1}{2}H_2)} - E°_{(Mg^{2+}/Mg)}$$

$$= 0 - E°_{(Mg^{2+}/Mg)} = -E°_{(Mg^{2+}/Mg)}$$

22. (i) For the given cell, the half-cell reactions will be given as below:

At anode $\quad Mg \longrightarrow Mg^{2+} + 2e^-$

At cathode $\quad Cu^{2+} + 2e^- \longrightarrow Cu$

Therefore, the overall cell reaction will be

$$Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu$$

The Nernst equation is

$$E_{cell} = E°_{cell} - \frac{0.0591}{n}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$\therefore \quad E_{cell} = [0.34 - (-2.36)] - \frac{0.0591}{2}\log\frac{(0.001)}{(0.0001)}$$

$$= 2.71 - 0.0295\log(10) = 2.7 - 0.0295$$

$$= 2.68\text{ V}$$

(ii) $Fe(s)\,|\,Fe^{2+}(0.001\,M)\,||\,H^+(1\,M)|\,H_2(g)\ (1\text{ bar})\,|\,Pt\,(s)$

$E_{cell} = 0.53$ V (approx)

Refer to above solution in (i)

23. $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

E_{cell} decreases when concentration of Zn^{2+} ions is increased. Refer to text on page 55.

24. $E_{cell} = 0.3125$V. Refer to solution 22 above.

Use $E_{cell} = E°_{cell} - \dfrac{0.059}{n}\log\dfrac{[Cu^{2+}]}{[Ag^+]^2}$

25. Since, oxidation of Cr is taking place in the given reaction, the chromium electrode is anode and Fe gets reduced in the reaction, so, Fe electrode is cathode.

The half-cell reactions are as follows

At anode $\quad Cr \longrightarrow Cr^{3+} + 3e^-] \times 2$

At cathode $\quad Fe^{2+} + 2e^- \longrightarrow Fe] \times 3$

Overall reaction

$$2Cr + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe$$

$$E°_{cell} = E_{cathode} - E_{anode} = -0.44 - (-0.74) = 0.3\text{ V}$$

$$E = E° - \frac{0.0591}{n}\log\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

Here, n = number of electrons transferred i.e. 6.

$$= 0.3 - \frac{0.0591}{6}\log\frac{(0.01)^2}{(0.1)^3} = 0.3098\text{ V} \approx 0.31\text{V}$$

26. Given, $E°_{Cd^{2+}/Cd} = -0.403$ V

$E°_{Zn^{2+}/Zn} = -0.763$V

$\therefore \quad E°_{Cell} = -0.403 - (-0.763)$

$E°_{Cell} = 0.36$ V

$\because \quad \Delta_r G° = -nFE°_{Cell}$

where n = number of moles of electrons used

$n = 2$ (Here)

$F = 96500\text{ C mol}^{-1}$

$\therefore \quad \Delta_r G° = -2 \times 96500 \times 0.36 = 69480$ J / mol

Also, $E°_{Cell} = \dfrac{0.0591}{n}\log K_C$

$$\therefore \quad \log K_C = \frac{n \times E°_{Cell}}{0.0591} = \frac{2 \times 0.36}{0.0591} = 12.18$$

$\log K_C = 12.18$

27. Since, $E°_{Ag^+/Ag} > E°_{Zn^{2+}/Zn}$, the zinc electrode is the anode. The half-cell reactions are as follows:

At anode $\quad Zn \longrightarrow Zn^{2+} + 2e^-$

At cathode $\quad Ag^+ + e^- \longrightarrow Ag$

Overall cell reaction is

$$Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag$$

$$E°_{cell} = E_{cathode} - E_{anode}$$

$$= 0.80\text{V} - (-0.76)\text{ V} = 1.56\text{ V}$$

$$\Delta G° = -nFE°_{cell}$$

$$= -2 \times 96500\text{ C mol}^{-1} \times 1.56\text{ V}$$

$$= -301080\text{ J mol}^{-1}$$

$$= -301.08\text{ kJ mol}^{-1}$$

28. $\Delta_r G° = -nFE°_{cell}, n = 6$

$= -6 \times 96500$ C/mol $\times 0.34$ V

$= -196860$ J/mol or -196.860 kJ / mol

$\therefore E°_{cell} = 0.059\text{ V}/n \times \log K_C$

$$\log K_C = \frac{0.34\text{ V} \times 6}{0.059\text{V}} = 34.5762$$

29. Refer to solution 28 [$E°_{cell} = 0.34$,V and $\Delta G° = -196.86$ kJ mol^{-1} and using the formula, $E°_{cell} = \dfrac{2.303\,RT}{nF}\log K$, K can be calculated.]

$$K = 3.192 \times 10^{34}$$

30. Two half reactions for the given redox reaction may be written as:

$$2Fe^{3+}(aq) + 2e^- \longrightarrow 2Fe^{2+}(aq)$$
$$2I^- \longrightarrow I_2 + 2e^-$$

2 moles of electrons are involved in the reaction, so $n = 2$

$$\Delta_r G^\circ = -nFE^\circ_{cell}$$
$$= -(2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.236 \text{ V})$$
$$= -45548 \text{ CV} = -45548 \text{ J}$$
$$\Delta_r G^\circ = -45.55 \text{ kJ}$$
$$\log K_C = -\frac{\Delta G^\circ}{2.303\,RT}$$
$$= -\frac{(-45.55 \text{ kJ})}{2.303 \times (8.314 \times 10^{-3} \text{kJ K}^{-1}) \times (298 \text{ K})} = 7.983$$
$$K_C = \text{antilog}(7.983) = 9.616 \times 10^7$$

31. (a) E° value of silver ($E^\circ_{Ag^+/Ag} = +0.80$ V) is lower than that of gold, hence silver displaces gold ($E^\circ_{Au^{3+}/Au} = +1.40$ V), which gets deposited on the silver object.

E° value of copper ($E^\circ_{Cu^{2+}/Cu} = +0.34$) is lower than that of silver, hence silver cannot displace copper from its solution.

(b) (i) Electrons flow from Zn to Ag plate.

(ii) Zn acts as anode and Ag acts as cathode

(iii) Cell will stop functioning

(iv) Concentration of Zn^{2+} ions will increase and that of Ag^+ ions will decrease.

(v) No change

32. Refer to text on page 51.

33. The reaction will be feasible, if emf of the cell reaction is positive.

(i) $Fe^{3+}(aq) + I^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}I_2$

$$E^\circ_{cell} = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{1/2\,I_2/I^-}$$
$$= 0.77 - 0.54$$
$$= 0.23 \text{ V (feasible)}$$

(ii) $2Ag^+(aq) + Cu(s) \longrightarrow 2Ag(s) + Cu^{2+}(aq)$

$$E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{2+}/Cu}$$
$$= 0.80 - 0.34 = 0.46 \text{ V (feasible)}$$

(iii) $Fe^{3+}(aq) + Br^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}Br_2$

$$E^\circ_{cell} = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{1/2\,Br_2/Br^-}$$
$$= 0.77 - 1.09$$
$$= -0.32 \text{ V (not feasible)}$$

(iv) $Ag(s) + Fe^{3+}(aq) \longrightarrow Ag^+(aq) + Fe^{2+}(aq)$

$$E^\circ_{cell} = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Ag^+/Ag}$$
$$= 0.77 - 0.80 = -0.03 \text{ V (not feasible)}$$

(v) $\frac{1}{2}Br_2(aq) + Fe^{2+}(aq) \longrightarrow Br^- + Fe^{3+}$

$$E^\circ_{cell} = E^\circ_{1/2\,Br_2/Br^-} - E^\circ_{Fe^{3+}/Fe^{2+}}$$
$$= 1.09 - 0.77 = 0.32 \text{ V (feasible)}$$

34. (i) Refer to solution 28 on page 61.
[$E^\circ_{cell} = +0.34$V, $\Delta_r G^\circ = -196.86$ kJ, $K_C = 3.17 \times 10^{34}$]

(ii) Refer to solution 28 on page 61
[$E^\circ_{cell} = +0.03$ V, $\Delta_r G^\circ = -2.895$ kJ, $K_C = 3.22$]

|TOPIC 2| Conductivity of Electrolytic Solution and Its Measurement

CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

Before introducing the concept of conductance of electricity through electrolytic solutions, we must revise few terms related to conductance of electricity which we have studied in physics.

Resistance It is defined as the hindrance provided by a conductor in the passage of current. Every substance offers resistance to the flow of electricity to a small or large extent. A substance which offers greater resistance will allow less electricity to flow through it. The electrical resistance, R of any object is directly proportional to its length, l and inversely proportional to its area of cross-section, A. Thus,

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho\frac{l}{A}$$

Here, ρ is resistivity (specific resistance) of the object.

Resistivity It is defined as the resistance offered by a substance of 1m length with area of cross-section equal to 1m^2.

Thus, resistivity $(\rho) = R\frac{A}{l}$

Units of resistivity = ohm $\times \frac{cm^2}{cm}$ = ohm cm or

Ω cm or Ω m in SI unit.

It can be seen that

$$1\ \Omega m = 100\ \Omega cm \text{ or } 1\ \Omega cm = 0.01\ \Omega m$$

IUPAC recommends the term resistivity over specific resistance.

Conductance The ease with which current flows through a conductor is known as its conductance (G). It is the inverse of resistance.

$$G = \frac{1}{R}$$

Thus, $$\frac{1}{R} = \frac{1}{\rho} \times \frac{1}{\frac{l}{A}} = \frac{1}{\rho}\frac{A}{l}$$

Substituting $\frac{1}{R}$ by G and $\frac{1}{\rho}$ by κ, we have the equation as:

$$G = \kappa \frac{A}{l}$$

The SI unit of conductance (G) is Siemens (S). It can be also written as $ohm^{-1} (\Omega^{-1})$ or mho.

Conductivity The inverse of resistivity is called conductivity, κ, also known as the specific conductance or conductivity. It can be defined as the conductance of a solution of 1m length with area of cross-section equal to $1 m^2$.

i.e. $G = \kappa$ (when, $l = 1$ m and $A = 1 m^2$)

$$\kappa = \frac{1}{\rho}$$

Units of conductivity (κ) = $\frac{1}{ohm \cdot cm} = ohm^{-1} cm^{-1}$

or $\Omega^{-1}\ cm^{-1}$

In SI units, l is expressed in m, area of cross-section in m^2 so that the unit of conductivity is $S\ cm^{-1}$.

(The SI unit of conductivity is $S\ m^{-1}$ but quite often, κ is expressed in $S\ cm^{-1}$. $1 S\ cm^{-1} = 100\ S\ m^{-1}$)

The magnitude of conduction depends upon the nature of the material. It also depends upon the temperature and pressure at which the measurements are made. Materials are classified into conductors, insulators and semiconductors. It depends on the magnitude of their conductivity.

Different Types of Materials

Conductors The substance which have very large conductivity are known as conductors, e.g. metals and their alloys, certain non-metals like carbon-black, graphite and some organic polymers are electronically conducting.

Metallic Conductors In metallic conductors, the flow of electricity takes place due to the flow of electrons only, i.e. no flow of matter. Thus, the matter does not decompose. Due to the vibration of Kernels, the electrical conduction decreases with decrease in temperature.

Electrolytic Conductors In electrolytic conductors, the flow of electricity takes place due to the flow of charge, i.e. matter decomposes into ions. The electrical conduction increases with increase of temperature due to increase in dissociation.

Insulators The substances which have very low conductivity are known as insulators, e.g. glass, ceramics, etc.

Semiconductors The substances which have conductivity between conductors and insulators are known as semiconductors, e.g. silicon, doped silicon and gallium arsenide.

Superconductors The substances which have zero resistivity or infinite conductivity, are known as superconductors, e.g. metals and their alloys at very low temperatures (0 to 15 K). Now a days, a number of ceramic materials and mixed oxides show superconductivity at temperatures as high as 150 K.

Electronic Conductance

Electrical conductance through metal is due to the movement of electrons and termed as electronic or metallic conductance. It depends upon the nature and structure of metal, number of valence electrons per atom and temperature (it decreases with increase of temperature).

Pure water has very low conductivity but when electrolytes are dissolved in water, they furnish their own ions in the solution, hence its conductivity increases. The conductance of electricity by ions which are present in the solutions is called **electrolytic** or **ionic conductance**.

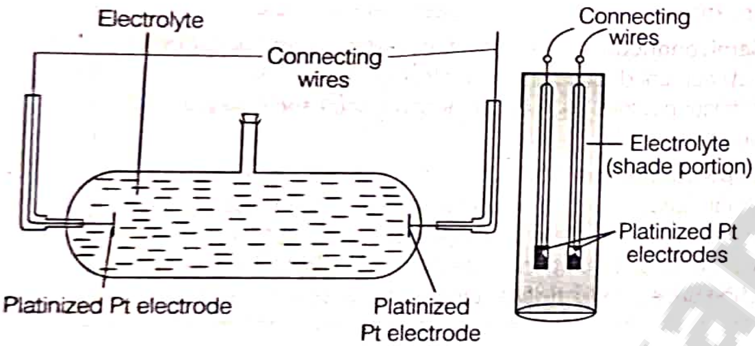
The conductivity of electrolytic solutions depends on the nature of the electrolyte, size of the ions produced and their solution, nature of the solvent and its viscosity, concentration of the electrolyte and temperature (it increases with the increase in temperature).

As the electrons enter at one end and go out through the other end, the composition of the metallic or electronic conductor remains unchanged. The mechanism of conductance through semiconductors is more complex. Passage of direct current through ionic solution over a prolonged period can lead to change in its composition due to electrochemical reactions.

Measurement of the Conductivity of Ionic Solutions

The unknown resistance of a conductor can be measured using Wheatstone bridge. However, the resistance of an ionic solution from which we calculate its conductance, will be difficult to measure.

Usually, we encounter two major problems. Firstly, passing direct current (DC) changes the composition of the solution. Secondly, a solution cannot be connected directly to the bridge. The first difficulty is resolved by using an alternating current (AC) and the second problem is solved by using a specially designed vessel called conductivity cell which has two platinum electrodes coated with platinum black as shown in figure.



Two different types of conductivity cells

The area of cross-section of these electrodes is A and they are separated by a distance, l. Thus, the resistance of column containing electrolytic solution between the electrodes is given by

$$R = \rho \frac{l}{A} \text{ or } R = \frac{1}{\kappa} \times \frac{l}{A}$$

The quantity $\frac{l}{A}$ is called the cell constant. It is denoted by the symbol G^*. The cell constant will be given by

$$G^* = \frac{l}{A} = R \times \kappa$$

Unit of cell constant $(G^*) = \text{m}^{-1}$

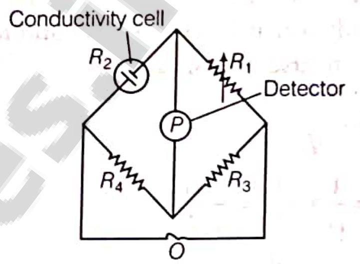
Measurement of Cell Constant

For measuring the cell constant, the resistance of the cell is measured with KCl solutions whose conductivity at different temperatures and concentrations is already known.

Then, the resistance of an electrolyte can be measured by using a cell that is based on Wheatstone bridge principle.

Measurement of Unknown Resistance

In the given figure, R_2 is the resistance of the electrolyte to be measured, R_3 and R_4 are known resistances and R_1 is the variable resistance which is adjusted until no current passes through the circuit. O is the source of AC power called oscillator. Under the no current condition, minimum or no sound can be heard from the earphone, P (a detector).



Arrangement for measurement of resistance of a solution of an electrolyte

When no current passes, $\frac{R_1}{R_2} = \frac{R_3}{R_4}$

Therefore, $R_2 = \frac{R_1 R_4}{R_3}$

Once the cell constant and the resistance of the electrolyte in the cell are known, the conductivity of the cell is given by,

$$\kappa = \frac{\text{Cell constant}}{R} = \frac{G^*}{R}$$

The conductivity of a solution depends upon the charge on the ions, size of the ions in which they dissociate, concentration of ions and the ease with which ions move in the solution under a potential gradient. In other words, the same electrolyte will show different conductivity at different temperatures and in different solvents.

Molar Conductivity

Molar conductivity of a solution is the conductance of solution containing one mole of electrolyte, kept between two electrodes having unit length between them and large cross-sectional area, so as to contain the electrolyte.

In other words, molar conductivity is the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross-section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. It is denoted by Λ_m.

$$\Lambda_m = \frac{\kappa}{C}$$

If κ is expressed in $\Omega^{-1}m^{-1}$ or Sm^{-1} unit and the concentration, C in mol m^{-3}, then the unit of Λ_m will be $\Omega^{-1}m^2mol^{-1}$ or $Sm^2\ mol^{-1}$.

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

where, M is the molarity of the electrolytic solution.

$$1\ Sm^2mol^{-1} = 10^4\ Scm^2mol^{-1}$$

$$\text{or, } 1\ Scm^2mol^{-1} = 10^{-4}\ Sm^2mol^{-1}$$

EXAMPLE |1| The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is $5.55 \times 10^3\ \Omega$. Calculate its resistivity, conductivity and molar conductivity. **All India 2012**

> (i) Calculate area from radius by using, $A = \pi r^2$
> (ii) Calculate resistivity from the formula, $\rho = \frac{RA}{l}$
> (iii) Calculate conductivity (κ) from resistivity as $\kappa = 1/\rho$
> (iv) Calculate molar conductivity, Λ_m by using the formula
> $$\Lambda_m = \frac{\kappa \times 1000}{M}$$

Sol. Area, $A = \pi r^2 = 3.14 \times \left(\frac{1}{2}\right)^2 cm^2 = 0.785\ cm^2$

Resistivity, $\rho = \frac{RA}{l}$

$$= \frac{5.55 \times 10^3 \Omega \times 0.785\ cm^2}{50\ cm} = 87.135\ \Omega\ cm$$

Conductivity, $\kappa = \frac{1}{\rho} = \frac{1}{87.135}\ \Omega^{-1}\ cm^{-1}$

$$= 0.01148\ \Omega^{-1}cm^{-1}$$

$$= 1.148 \times 10^{-2}\ S\ cm^{-1}$$

Molar conductivity,

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.148 \times 10^{-2} \times 1000}{0.05}$$

$$= 229.6\ S\ cm^2\ mol^{-1}$$

Variation of Conductivity and Molar Conductivity with Concentration

Conductivity always decreases with decrease in concentration (i.e. with dilution) of both the strong and weak electrolytes. This is due to the fact that the number of ions that carry current in a unit volume of solution always decreases with decrease in concentration. The conductivity of a solution is the conductance of a unit volume of the solution, kept between two platinum electrodes with unit area of cross-section and at a distance of unit length. The molar conductivity is the conductance of that volume of the solution which contains one mole of the electrolyte. Conductivity is expressed as, $G = \frac{\kappa A}{l} = \kappa$ (both A and l are unity in their appropriate units in m or cm) while molar conductivity is expressed as $\Lambda_m = \kappa V$

It is because $\Lambda_m = \frac{\kappa A}{l}$ $\because$ $l = 1$ and $A = V$

[volume containing 1 mole of electrolyte]

Molar conductivity increases with decrease in concentration (i.e. with dilution). This is because the total volume V of solution containing one mole of electrolyte increases.

Note

When the concentration approaches zero, the molar conductivity reaches a limiting value, known as **limiting molar conductivity** and is denoted as Λ_m°.

Variation in Λ_m with Concentration (for Strong and Weak Electrolytes)

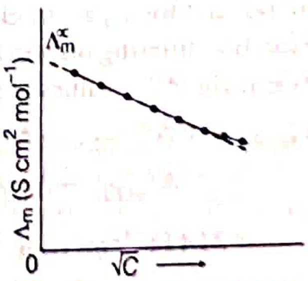
For Strong Electrolytes

Practically strong electrolytes completely dissociate at all concentrations. For strong electrolytes, Λ_m increases slowly with dilution. This can be represented by equation, Debye-Huckel-Onsager equation.

$$\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$$

If we plot Λ_m against $\sqrt{C}$, we get a straight line with slope as '$-A$' and intercept as 'Λ_m°'. The value of constant A depends upon the type of electrolyte. i.e. the charges on the cation and anion produced on the dissociation of electrolyte in the solution.

Thus, $NaCl, CaCl_2, MgSO_4$ are known as 1-1, 2-1 and 2-2 electrolytes, respectively. All electrolytes of a particular type have the same value of A.



Variation of Λ_m with $\sqrt{C}$ for KCl (strong electrolyte).

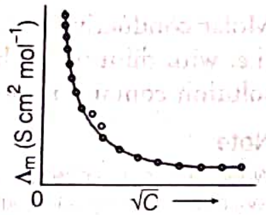
For Weak Electrolytes

The electrolytes which do not ionise completely in aqueous as well as in molten state are called weak electrolytes, e.g. H_2CO_3, CH_3COOH, etc.

A weak electrolyte (like acetic acid) is not completely dissociated at all concentrations. With dilution, the degree of dissociation increases, resulting in increase in the number of

ions. In case of weak electrolytes, the Λ°_m value increases steeply with dilution, especially in the low concentration region. In this region, the graph of weak electrolytes in a plot of Λ_m against $\sqrt{C}$ becomes parallel to the Y-axis. So, the limiting molar conductivity of a weak electrolyte cannot be determined by extrapolation of the plot. At infinite dilution ($C \rightarrow$ zero) electrolyte dissociates completely ($\alpha = 1$), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately.

It is rather determined by applying the Kohlrausch law of independent migration of ions. Through Kohlrausch law, we can determined Λ°_m values of weak electrolyte (discussed later in this chapter).



Variation of Λ_m with $\sqrt{C}$ for weak electrolyte (CH_3COOH).

Degree Of Dissociation

The ratio of molar conductivity (Λ_m) at a specific concentration (C) to the molar conductivity at infinite dilution, i.e. limiting molar conductivity, Λ°_m is known as degree of dissociation.

At any concentration C, if α is the degree of dissociation, then for a weak electrolyte, $\alpha = \dfrac{\Lambda_m}{\Lambda^\circ_m}$

Since, for a weak electrolyte,

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = \frac{C\Lambda_m^2}{(\Lambda^\circ_m)^2\left(1 - \dfrac{\Lambda_m}{\Lambda^\circ_m}\right)} = \frac{C\Lambda_m^2}{\Lambda^\circ_m\,(\Lambda^\circ_m - \Lambda_m)}$$

KOHLRAUSCH LAW

Kohlrausch examined Λ°_m values for a number of strong electrolytes and found that for a pair of electrolytes with the same negative ion but differing only in the positive ion, the difference between the Λ°_m values is constant.

e.g. $\Lambda^\circ_{m(KCl)} - \Lambda^\circ_{m(NaCl)} = \Lambda^\circ_{m(KBr)} - \Lambda^\circ_{m(NaBr)}$

$= \Lambda^\circ_{m(KI)} - \Lambda^\circ_{m(NaI)}$

$= 23.4\ \Omega^{-1}cm^2mol^{-1}\ (S\ cm^2 mol^{-1})$

Similarly, with a common cation, the difference between Λ°_m values is also found constant.

$\Lambda^\circ_{m(KBr)} - \Lambda^\circ_{m(KCl)} = \Lambda^\circ_{m(NaBr)} - \Lambda^\circ_{m(NaCl)}$

$= 1.8\ \Omega^{-1}cm^2mol^{-1}\ \ (S cm^2 mol^{-1})$

The above observation led to formulate the **Kohlrausch law of independent migration of ions.**

It states that *"limiting molar conductivity of an electrolyte is the sum of the individual contributions of the cation and the anion of the electrolyte".*

e.g. $\Lambda^\circ_{m\,(NaCl)} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$

where, $\Lambda^\circ_{m\,(NaCl)}$ is the molar conductivity of NaCl and $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are limiting molar conductivity of sodium and chloride ions respectively.

In general, if an electrolyte produces ν_+ cations and ν_- anions, the above equation becomes

$$\Lambda^\circ_m = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$$

Applications of Kohlrausch Law

Some important applications of Kohlrausch law are as follows :

(i) The molar conductivity of weak electrolytes at infinite dilution can be calculated by using Kohlrausch's law.

(ii) Degree of dissociation of weak electrolyte (like acetic acid) at a given concentration can be calculated.

(iii) Knowing the degree of dissociation (α), the dissociation constant (K) of the weak electrolyte at a given concentration of the solution, can be calculated.

(iv) Solubility of sparingly soluble salts can be calculated as

solubility $= \dfrac{\kappa \times 1000}{\Lambda^\circ_m}$ (mol / L)

EXAMPLE |2| Calculate Λ°_m for acetic acid,

Given that, $\Lambda^\circ_{m\,(HCl)} = 426\ S\ cm^2\ mol^{-1}$

$\Lambda^\circ_{m\,(NaCl)} = 126\ S\ cm^2\ mol^{-1}$

$\Lambda^\circ_{m\,(CH_3COONa)} = 91\ S\ cm^2\ mol^{-1}$ **Delhi 2010**

Sol. $\Lambda^\circ_{m\,(CH_3COOH)} = \Lambda^\circ_{H^+} + \Lambda^\circ_{CH_3COO^-}$

$= \Lambda^\circ_{H^+} + \Lambda^\circ_{Cl^-} + \Lambda^\circ_{CH_3COO^-} + \Lambda^\circ_{Na^+} - \Lambda^\circ_{Cl^-} - \Lambda^\circ_{Na^+}$

$= \Lambda^\circ_{m\,(HCl)} + \Lambda^\circ_{m\,(CH_3COONa)} - \Lambda^\circ_{m\,(NaCl)}$

$= (426 + 91 - 126)\ S\ cm^2\ mol^{-1}$

$= 391\ S\ cm^2\ mol^{-1}$

EXAMPLE |3| Conductivity of 0.00241 M acetic acid solution is $7.896 \times 10^{-5} S\ cm^{-1}$.

Calculate its molar conductivity in this solution. If Λ°_m for acetic acid be $390.5\ S\ cm^2\ mol^{-1}$, what would be its dissociation constant? **NCERT Delhi 2008; All India 2008**

(i) First, find molar conductivity using the formula, $\Lambda^C_m = \dfrac{\kappa \times 1000}{C}$

(ii) Then, find degree of dissociation (α) and dissociation constant (K_a) by using formula, $\alpha = \dfrac{\Lambda^C_m}{\Lambda^\circ_m}$ and $K_a = \dfrac{C\alpha^2}{1-\alpha}$, respectively.

Sol. Given, $\kappa = 7.896 \times 10^{-5}$ S cm^{-1},

$\Lambda^{\circ}_{m\,(CH_3COOH)} = 390.5$ S cm^2 mol^{-1}

and Molarity $(M) = 0.00241$ M

Molar conductivity,

$$\Lambda^C_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{7.896 \times 10^{-5}\,\text{S cm}^{-1} \times 1000}{0.00241\,\text{M (mol cm}^{-3})}$$

$$\Lambda^C_m = 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

Degree of dissociation,

$$\alpha = \frac{\Lambda^C_m}{\Lambda^{\circ}_m} = \frac{32.76}{390.5} = 8.4 \times 10^{-2}$$

For dissociation constant of acetic acid, CH_3COOH

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

	CH_3COOH	CH_3COO^-	H^+
Initial conc.	C	0	0
After time t,	$C - C\alpha$	$C\alpha$	$C\alpha$

Dissociation constant,

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$= \frac{C\alpha^2}{1-\alpha}$$

$$K_a = \frac{0.00241\,(8.4 \times 10^{-2})^2}{(1-0.084)} = 1.86 \times 10^{-5}$$

TOPIC PRACTICE 2

OBJECTIVE Type Questions

1. Select the appropriate statement(s) about ionic conductance.

(a) It is the conductance of electricity by ions present in the solutions

(b) It depends on nature of solvent, its viscosity and concentration of electrolyte

(c) It depends upon the size of ions produced and solvation

(d) All of the above

2. At 25°C the specific conductivity of $N/50$ KCl solution is 0.002765 mho cm^{-1}, the resistance of cell with solution is 400 Ω then cell constant (π) will be

(a) 0.533 cm^{-1} (b) 1.106 cm^{-1}

(c) 2.212 cm^{-1} (d) None of these

3. Unit of specific conductance is

(a) cm^{-2}ohm^{-1} (b) cm ohm^{-1}equivalent^{-1}

(c) cm^{-1}ohm^{-1} (d) cm^{-2} ohm

4. The conductance of electrolytic solution kept between the electrodes of conductivity cell at unit distance but having area of cross-section large enough to accommodate sufficient volume of solution is called

(a) limiting molar conductivity

(b) molar conductivity

(c) conductivity

(d) All of the above

5. Which of the following option will be the limiting molar conductivity of CH_3COOH if the limiting molar conductivity of CH_3COONa is 91 S cm^{2}mol^{-1}? Limiting molar conductivity for individual ions are given in the following table. **CBSE SQP 2021**

S.No.	Ions	Limiting molar conductivity/ S cm^{2}mol^{-1}
1	H^+	349.6
2	Na^+	50.1
3	K^+	73.5
4	OH^-	199.1

(a) 350 Scm^{2}mol^{-1} (b) 375.3 Scm^{2}mol^{-1}

(c) 390.5 Scm^{2}mol^{-1} (d) 340.4 Scm^{2}mol^{-1}

6. Two electrolytes X and Y are diluted. Λ_m of Y increases 1.5 times and for X it increases 25 times. Predict the strong electrolyte among X and Y.

(a) X

(b) Y

(c) Both (a) and (b)

(d) There is no effect of dilution on nature of electrolyte

7. The resistance of the cell containing KCl solution at 23°C was found to be 55 Ω. Its cell constant is 0.616 cm^{-1}. The conductivity of KCl solution (Ω^{-1} cm^{-1}) is

(a) 1.21×10^{-3} (b) 1.12×10^{-2} (c) 1.12×10^{-3} (d) 1.21×10^{-2}

8. Kohlrausch give the following relation for strong electrolytes :

$$\wedge = \wedge_0 - A\sqrt{C}$$

Which of the following equality holds? **Delhi 2020**

(a) $\wedge = \wedge_0$ as $C \longrightarrow \sqrt{A}$ (b) $\wedge = \wedge_0$ as $C \longrightarrow \infty$

(c) $\wedge = \wedge_0$ as $C \longrightarrow 0$ (d) $\wedge = \wedge_0$ as $C \longrightarrow 1$

VERY SHORT ANSWER Type Questions

9. Why alternating current is used for measuring resistance of an electrolytic solution? **NCERT Exemplar**

10. Why does the conductivity of a solution decreases with dilution? **NCERT Intext**

11. Suggest a way to determine the Λ_m° value of water. **NCERT Intext**

12. The conductivity of 0.20 M solution of KCl, at 298 K, is 0.0248 S cm^{-1}. Calculate its molar conductivity. **NCERT; Delhi 2013**

SHORT ANSWER Type I Questions

13. Solutions of two electrolytes '*A*' and '*B*' are diluted. The Λ_m of '*B*' increases 1.5 times while that of *A* increases 25 times. Which of the two is a strong electrolyte? Justify your answer. Graphically show the behavior of '*A*' and '*B*'. **CBSE SQP (Term II)**

14. Calculate the degree of dissociation (α) of acetic acid, if its molar conductivity (Λ_m) is 39.05 S cm^2 mol^{-1}.
Given : $\lambda^0(H^+) = 349.6$ S cm^2 mol^{-1}
and λ^0 $(CH_3COO^-) = 40.9$ S cm^2 mol^{-1} **Delhi 2017**

15. The conductivity of 0.001 M acetic acid is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm^2/mol. **Delhi 2013 C**

16. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant, if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}? **Delhi 2012; NCERT**

17. Explain with a graph, the variation of molar conductivity of a strong electrolyte with dilution. **All India 2019**

18. Write the slope value obtained in the plot of log $[R_0]/[R]$ *vs* time for a first order reaction. **Delhi 2020**

SHORT ANSWER Type II Questions

19. The resistance of a conductivity cell, when filled with 0.05 M solution of an electrolyte *x*, is 100 Ω at 40°C. The same conductivity cell filled with 0.01 M solution of electrolyte *y*, has a resistance of 50 Ω. The conductivity of 0.05 M solution of electrolyte *x* is 1.0×10^{-4} S cm^{-1}.
Calculate
(i) cell constant.
(ii) conductivity of 0.01 M *y* solution
(iii) molar conductivity of 0.01 M *y* solution **All India 2008 C**

20. Represent the cell in which the following reaction takes place. The value of E° for the cell is 1.260 V. What is the value of E_{cell}?
$$2Al(s) + 3Cd^{2+}(0.1 M) \longrightarrow 3Cd(s) + 2Al^{3+}(0.01 M)$$
CBSE SQP (Term II)

21. Conductivity of 2.5×10^{-4} M methanoic acid is 5.25×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation.
Given: $\lambda^\circ(H^+) = 349.5$ S cm^2 mol^{-1} and $\lambda^\circ(HCOO^-) = 50.5$ S $cm^2 mol^{-1}$. **All India 2015**

LONG ANSWER Type Questions

22. (i) What is limiting molar conductivity? Why there is steep rise in the molar conductivity of a weak electrolyte on dilution?
(ii) Calculate the emf of the following cell at 298 K :
$Mg(s) | Mg^{2+}$ (0.1 M) || $Cu^{2+}(1.0 \times 10^{-3}$ M) | Cu(s)
[Given = E°_{cell} = 2.71 V] **Delhi 2017 C**

23. (i) The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}.
Calculate its molar conductivity and degree of dissociation (α). Given,
$\lambda^\circ(H^+) = 349.6$ S $cm^2 mol^{-1}$ and
$\lambda^\circ(CH_3COO^-) = 40.9$ Scm^2mol^{-1}.
(ii) Define electrochemical cell. What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell? **All India 2016**

24. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration. **NCERT**

25. The conductivity of NaCl at 298 K has been determined at different concentrations and the results are given below.

Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^{-2} \times \kappa$ /Sm^{-1}	1.237	11.85	23.15	55.53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $C^{1/2}$. Find the value of Λ_m°.

26. (i) State Kohlrausch law.

(ii) Calculate the emf of the following cell at 298 K:

$Al(s)|Al^{3+}$ (0.15M) || Cu^{2+} (0.025 M|Cu(s)

(Given: $E^{\circ}_{(Al^{3+}/Al)} = -1.66V$, $E^{\circ}_{(Cu^{2+}/Cu)} = 0.34V$

log 0.15 = −0.8239, log 0.025 −1.6020)

Or **CBSE SQP 2021**

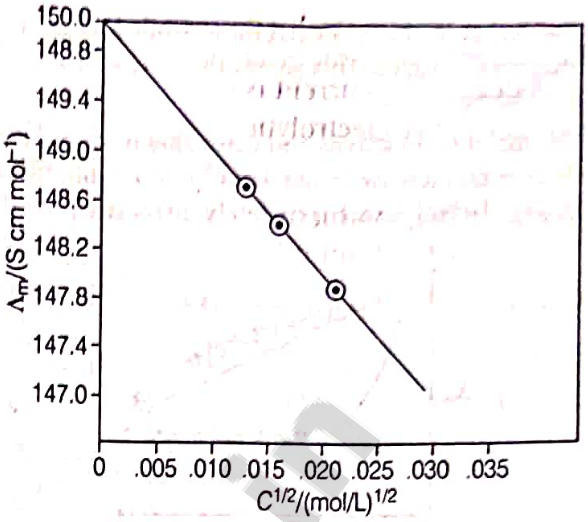
(i) On the basis of E° values, identify which amongst the following is the strongest oxidising agent?

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-;\ E^{\circ} = +1.36\ V$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O;\ E^{\circ} = 1.51V$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O;\ E^{\circ} = +1.33\ V$$

(ii) The following figure 2, represents variation of (Λ_m) *vs* $\sqrt{C}$ for an electrolyte. Here Λ_m is the molar conductivity and *C* is the concentration of the electrolyte.



(a) Define molar conductivity.

(b) Identify the nature of electrolyte on the basis of the above plot. Justify your answer.

(c) Determine the value of Λ_m for the electrolyte.

(d) Show how to calculate the value of *A* for the electrolyte using the above graph.

HINTS AND EXPLANATIONS

1. (*d*) The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. It depends on the nature of electrolyte added, size of ions produced and their solvation, nature of solvent and its viscosity, concentration of electrolyte and temperature (it increases with increase of temperature).

2. (*b*) Cell constant $(\pi) = R \times \kappa$

$$= (400\ \Omega) \times (0.002765\ \text{mho cm}^{-1})$$

$$= 1.106\ \text{cm}^{-1}$$

3. (*c*) Specific conductance $(k) = \frac{1}{\rho}$ and $\rho = \frac{R \cdot A}{l}$

$$\therefore \quad \kappa = \frac{1}{R} \cdot \frac{l}{A} = \text{cm}^{-1}\text{ohm}^{-1}$$

4. (*b*) Molar conductivity.

5. (*c*) Given, $\Lambda^{\circ}_{m(H^+)} \to 349.6\ \text{S cm}^2\text{mol}^{-1}$

$$\Lambda^{\circ}_{m(Na^+)} \to 50.1\ \text{S cm}^2\text{mol}^{-1}$$

$$\Lambda_{m(K^+)} \to 73.5\ \text{S cm}^2\text{mol}^{-1}$$

$$\Lambda_{m(OH^-)} \to 199.1\ \text{S cm}^2\text{mol}^{-1}$$

$$\Lambda_{(CH_3COONa)} \to 91\ \text{S cm}^2\text{mol}^{-1}$$

Complete reaction is as follows :

$$CH_3COONa + HCl \longrightarrow NaCl + CH_3COOH$$

$$\Lambda^{\circ}_m(CH_3COOH) = \Lambda^{\circ}_m(CH_3COONa) - \Lambda^{\circ}_m(Na^+) + \Lambda^{\circ}_m(H^+)$$

$$= 91 - 501 + 349.6$$

$$\Rightarrow 390.5\ \text{S cm}^2\text{mol}^{-1}$$

6. (*b*) *Y* is strong electrolyte because on dilution number of ions remains almost the same in case of strong electrolyte. Only interionic attraction decreases and increase in Λ_m is small.

7. (*b*) Conductivity, $\kappa = \frac{\text{Cell constant}}{\text{Resistance}} = \frac{0.616}{55}$

$$= 1.12 \times 10^{-2}\Omega^{-1}\ \text{cm}^{-1}$$

8. (*c*) When the concentration $(\lambda = \lambda_0)$ approaches zero (i.e, $C_0 \longrightarrow 0$), the molar conductivity reaches a limiting value known as limiting molar conductivity (Λ°_m). Thus, among the given option, *c* is correct.

9. Alternating current is used in electrolysis, so that concentration of ions in the solution remains constant and exact value of resistance is measured.

10. When the concentration (dilution) is decreased, the number of ions per unit volume carrying the current decreases on dilution, so conductivity always decreases with decrease in concentration.

11. The molar conductance of water at infinite dilution can be obtained from the knowledge of molar conductances at infinite dilution of sodium hydroxide, hydrochloric acid and sodium chloride (all strong electrolytes). This is in accordance with Kohlrausch's law.

$$\Lambda^{\circ}_{m(H_2O)} = \Lambda^{\circ}_{m(NaOH)} + \Lambda^{\circ}_{m(HCl)} - \Lambda^{\circ}_{m(NaCl)}$$

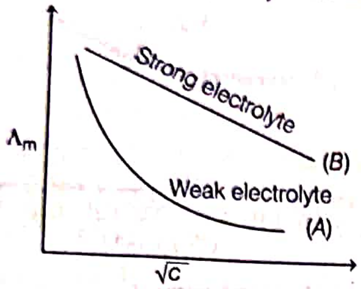
12. Molar conductivity,

$$\Lambda^C_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{0.0248\ \text{Scm}^{-1} \times 1000}{0.20\ \text{M (mol cm}^{-3})}$$

$$= 124\ \text{S cm}^2\ \text{mol}^{-1}$$

13. The Λ_m of 'B' increases 1.5 times while that of A increases 25 times. This shows that B is a strong electrolyte.

The molar conductivity increases slowly with dilution as there is no increase in number of ions on dilution as strong electrolyte are completely dissociated.



14. Kohlrausch's law,

$$\Lambda^\circ_m\ (CH_3COOH) = \lambda^\circ(H^+) + \lambda^\circ(CH_3COO^-)$$
$$= 349.6\ S\ cm^2\ mol^{-1} + 40.9\ S\ cm^2\ mol^{-1}$$
$$= 390.5\ S\ cm^2\ mol^{-1}$$
$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{39.05\ S\ cm^2\ mol^{-1}}{390.5\ S\ cm^2\ mol^{-1}},\ \alpha = 0.1$$

15. Refer to Example 3 on pages 66 and 67.
$[K_a = 1.18 \times 10^{-5}]$

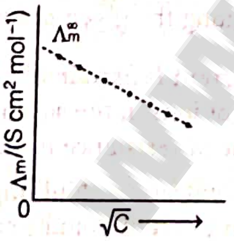
16. Given, conductivity, $\kappa = 0.146 \times 10^{-3}\ S\ cm^{-1}$

Resistance, $R = 1500\ \Omega$

$\therefore$ Cell constant $= \kappa \times R$
$$= 0.146 \times 10^{-3} \times 1500 = 0.219\ cm^{-1}$$

17. Strong electrolytes are completely ionised in all concentrations. For strong electrolytes, Λ_m increases slowly with dilution. It is found to vary with concentration according to the Debye-Huckel-Onsager equation.

$$\Lambda_m = \Lambda^\infty_m - [A + B\Lambda^\infty_m]\sqrt{C}$$



where, A and B are called Debye-Huckel constants.

If solution is diluted (concentration is decreased), there is decrease in ionic attractions hence, molar conductivity increases with decrease in concentration.

18. Slope $= \frac{k}{2.303}$

19. (i) Cell constant, $G^* =$ Resistance $(R) \times$ conductivity (k)
$$= 100 \times 1.0 \times 10^{-4} = 10^{-2}\ cm^{-1}$$

(ii) Conductivity of solution y,
$$\kappa = \frac{\text{Cell constant}}{\text{Resistance}} = \frac{10^{-2}}{50} = 2 \times 10^{-4}\ S\ cm^{-1}$$

(iii) Molar conductivity of solution y,
$$\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{2 \times 10^{-4} \times 1000}{0.01} = 20\ S\ cm^2\ mol^{-1}$$

20. Representation of the given cell is as follows
$$Al(s)\,|\,Al^{3+}(0.01\ M)\,||\,Cd^{2+}(0.1\ M)\,|\,Cd(s)$$

Given, $E^\circ = 1.26\ V$

In this case, cell potential is given by the following equation.
$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[Al^{3+}]^2}{[Cd^{2+}]^3}$$
$$E_{cell} = 1.26 - \frac{0.059}{6}\log\frac{(0.01)^2}{(0.1)^3}$$
$$= 1.26 - \frac{0.059}{6}(-1) = 1.26 + 0.009 = 1.269\ V$$

21. Refer to example 3 on pg 66 and 67 $[\Lambda_m = 210\ S\ cm^2 mol^{-1},$
$\Lambda^\circ_m = 400\ S\ cm^2\ mol^{-1}, \alpha = 0.525]$

22. (i) When concentration approaches zero, the molar conductivity is known as **limiting molar conductivity**. The change in Λ_m with dilution is due to the increase in the degree of dissociation and consequently the number of ions in the total volume of the solution that contains 1 mol of electrolyte, hence Λ_m increases steeply.

(ii) $$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$
$$= 2.71\ V - \frac{0.059}{2}\log\frac{0.1}{0.001}$$
$$= 2.71\ V - \frac{0.059}{2}\log 10^2 = 2.651\ V$$

23. (i) Given: Conductivity of CH_3COOH solution,
$$\kappa = 3.905 \times 10^{-5}\ S\ cm^{-1}$$

Concentration of CH_3COOH solution, $C = 0.001\ mol\ L^{-1}$,

Molar conductivity,
$$\lambda_m = \kappa \times \frac{1000}{C}$$
$$= \frac{(3.905 \times 10^{-5}\ S\ cm^{-1}) \times (1000\ cm^3\ L^{-1})}{0.001\ mol\ L^{-1}}$$
$$= 39.05\ S\ cm^2\ mol^{-1}$$

Molar conductivity at infinite dilution (λ°_m) for CH_3COOH,
$$\lambda^\circ_{m\,CH_3COOH} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$$
$$= 40.9 + 349.6 = 390.5\ S\ cm^2\ mol^{-1}$$

Degree of dissociation,
$$\alpha = \frac{\lambda_m}{\lambda^\circ_m} = \frac{39.05\ S\ cm^2\ mol^{-1}}{390.5\ S\ cm^2\ mol^{-1}} = 0.1$$

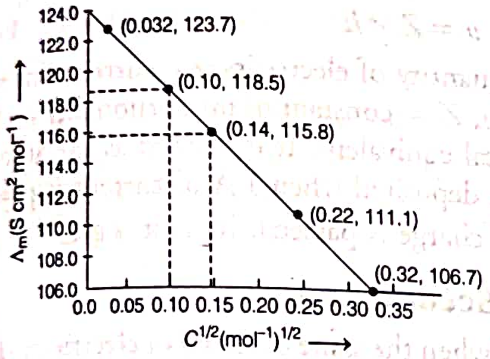
(ii) Refer to text on pages 50 and 51.

24. Refer to text on pages 63, 64 and 65.

25. According to the question, the given values are $1\ S\ cm^{-1} = 100\ S\ m^{-1}$ or $\dfrac{1\ S\ cm^{-1}}{100\ S\ m^{-1}} = 1$ (unit conversion factor)

Concentration (M)	κ ($S\ m^{-1}$)	κ ($S\ cm^{-1}$)	$\Lambda_m = \dfrac{1000 \times \kappa}{\text{molarity}}$ ($S\ cm^2\ mol^{-1}$)	$C^{1/2}$ ($M^{1/2}$)
10^{-3}	1.237×10^{-2}	1.237×10^{-4}	$\dfrac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = 123.7$	0.0316
10^{-2}	11.85×10^{-2}	11.85×10^{-4}	$\dfrac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = 118.5$	0.100
2×10^{-2}	23.15×10^{-2}	23.15×10^{-4}	$\dfrac{1000 \times 23.15 \times 10^{-4}}{2 \times 10^{-2}} = 115.8$	0.141
5×10^{-2}	55.53×10^{-2}	55.53×10^{-4}	$\dfrac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = 111.1$	0.224
10^{-1}	106.74×10^{-2}	106.74×10^{-4}	$\dfrac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = 106.7$	0.316

So, the graph between Λ_m and $C^{1/2}$ is shown



$\Lambda_m°$ = Intercept on the Λ_m axis = 124.0 S cm² mol⁻¹ (the value of Λ_m on extrapolation to zero concentration).

Or (i) MnO_4 is the strongest oxidising agent. Oxidising power of metals decreases with a increase in their $E°$ values.

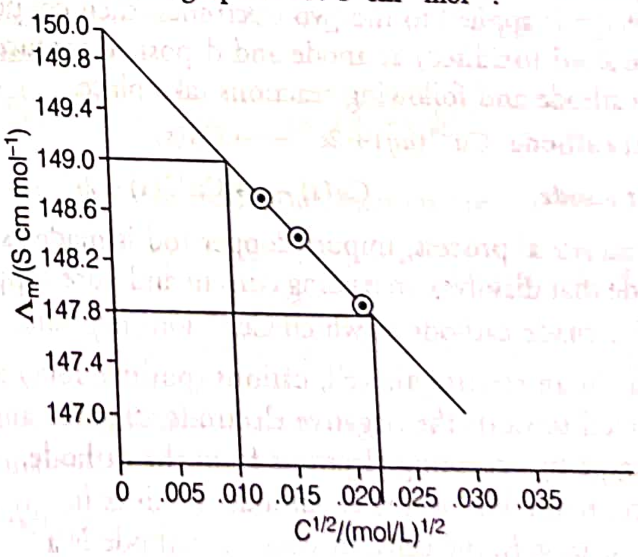
(ii) (a) Molar conducivity of a solution is the conductance of that volume of solution containing one mole of electrolyte, kept between two electrodes having unit length between them and large cross-sectional areas so as to contain the electrolyte.

(b) The nature the electrolyte on the basis of plot is strong electrolyte. For strong electrolyte, $\Lambda°_m$ increases slowly with dilution.

(c) Using Debye-Huckel Onsager equation,

$$\Lambda_m = \Lambda°_m - A\sqrt{C}$$

(d) $\Lambda°$ value from graph is 150 S cm² mol⁻¹.



$$A = -\text{slope} = \left(\frac{y_2 - y_1}{x_2 - x_1}\right)$$

$$= -\frac{(149 - 147.8)}{(0.010 - 0.022)}$$

$$= 100\ S\ cm^2 mol^{-1} / (mol/L^{-1})^{1/2}$$

26. (i) **Kohlrausch law** It states that limiting molar conductivity of an electrolyte is the sum of the individual contributions of the cation and the anion of the electrolyte.

Kohlraush examined $\Lambda°m$ values for a number of strong electrolytes and found that for a pair of electrolytes with the same negative ion but differing only in the positive ion. the difference between the $\Lambda°_m$ values is constant.

(ii) $E°_{cell} = E°_{cathode} - E°_{anode}$

$= 0.34 - (-1.66) = 2.00\ V$

According to Nernst equation,

$$E_{cell} = E°_{cell} - \frac{0.059}{n}\log\frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$$

Here, $n = 6$

$$E_{cell} = 2 - \frac{0.059}{6}\log\frac{[0.15]^2}{[0.025]^3}$$

$$= 2 - \frac{0.059}{6}(2\log 0.15 - 3\log 0.025)$$

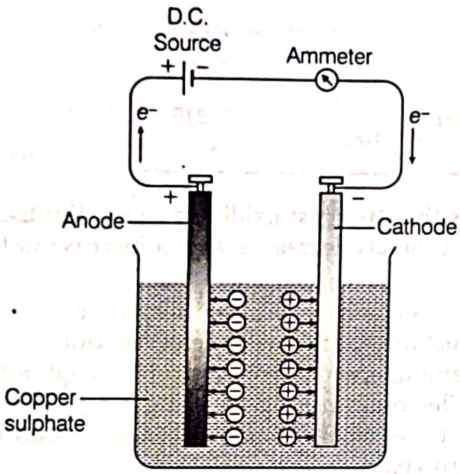
$$= 2 - \frac{0.59}{6}(-1.6478 + 4.8062)$$

$$= 2 - 0.0311 = 1.9689\ V$$

|TOPIC 3| Electrolytic Cells and Electrolysis

ELECTROLYTIC CELLS

Electrolytic cells are those cells in which electrical energy is used to carry out non-spontaneous chemical reactions and the reactions taking place in an electrolytic cell is called electrolysis. The apparatus used to bring about electrolysis is shown in the figure given below.



Electrolytic cell

In an electrolytic cell, external source of voltage is used to bring about a chemical reaction. One of the simplest electrolytic cell consists of two copper strips (which acts as anode and cathode) dipping in an aqueous solution of copper sulphate. When a DC voltage is applied to the two electrodes, then copper is dissolved (oxidised) at anode and deposited (reduced) at cathode and following reactions take place.

At cathode, $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

At anode, $Cu(s) \longrightarrow Cu^{2+}(s) + 2e^-$

In industrial process, impure copper rod is made as an anode that dissolves on passing current and pure copper rod is made cathode at which Cu^{2+} ions deposits.

Thus, in an electrolytic cell, cations (positive ions) are attracted towards the negative electrode, cathode and discharge by accepting electrons from the cathode. Hence, reduction occurs at cathode. (This is in contrast to galvanic cells, in which a cathode is a positive electrode). The anode in an electrolytic cell is positive electrode where oxidation of anions (negative ions) occurs.

Application of Electrolytic Cells

Many metals, e.g. Na, Mg, Al, etc., are produced on large scale by electrochemical reduction of their respective cations where no suitable chemical reducing agents are available for this purpose.

Faraday's Laws of Electrolysis

The quantitative aspect of electrolysis was studied extensively by Michael Faraday and his laws of electrolysis are known as Faraday's laws of electrolysis.

Faraday's First Law

It states that "the amount of chemical reaction occurring at any electrode by passing current is directly proportional to the quantity of electricity passed through the electrolyte (in solution or in molten state)".

Thus, w g of the substance gets deposited on passing Q coulomb of electricity.

$$w \propto Q \quad \text{or} \quad w = ZQ$$

$$w = Z \times it \qquad (\because Q = it)$$

where, Q = quantity of electricity, i = current (in A), t = time (in s), Z = constant of proportionality called electrochemical equivalent. It is defined as the amount of the substance deposited when 1 A of current is passed for 1 sec (1 C of charge is passed). Its unit is g C^{-1}.

Faraday's Second Law

It states that "when the same quantity of electricity is passed through different electrolytes, the amounts of different substances formed are directly proportional to their equivalent weights (i.e. atomic mass of the metal divided by the number of electrons required to reduce a cation of the metal)".

$$\boxed{\frac{w_1}{E_1} = \frac{w_2}{E_2} = \frac{w_3}{E_3} = \ldots}$$

where, w is the mass of substance and E is its equivalent weight.

Faraday's Constant

The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction. e.g. $Ag^+(aq) + e^- \longrightarrow Ag(s)$

One mole of the electron is required for the reduction of one mole of silver ions. The charge on an electron is 1.602×10^{-19}C. Therefore, the charge on one mole of electrons is $N_A \times 1.6021 \times 10^{-19}$C

$$= 6.02 \times 10^{23} \text{ mol}^{-1} \times 1.6021 \times 10^{-19}\text{C}$$

$$\text{Charge} = 96487 \text{ C mol}^{-1} \approx 96500 \text{ C mol}^{-1}.$$

This quantity of electricity is called Faraday's constant and is represented by the symbol F.

Note Combining Faraday's laws, we get, $Z = \frac{E}{F} = \frac{W}{Q}$.

EXAMPLE |1| An aqueous solution of copper sulphate, $CuSO_4$ was electrolysed between platinum electrodes using a current of 0.1287 A for 50 min.

[Given atomic mass of Cu = 63.5 g mol^{-1}]

(i) Write the cathodic reaction.

(ii) Calculate

(a) electric charge passed during electrolysis.

(b) mass of copper deposited at the cathode.

[Given, 1F = 96500 C mol^{-1}] **All India 2011C**

(i) Cathode is the site of reduction.

(ii) Use $Q = it$ to find the amount of charge passed and $m = Zit = \frac{\text{Equivalent weight} \times it}{96500}$

to find the mass of copper deposited.

Sol. Given that, $t = 50 \times 60 = 3000$ s, $i = 0.1287$A.

(i) $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

(ii) (a) $Q = it = 0.1287 \times 3000 = 386.1$ C

(b) $m = Z \times i \times t = \frac{\text{Eq. wt.}}{96500} \times i \times t$

$$= \frac{63.5}{2 \times 96500} \times 386.1 = 0.127 \text{ g}$$

Products of Electrolysis

The products of electrolysis depend on the following:

(i) nature of material being electrolysed.

(ii) type of electrodes being used. If the electrode is inert, it does not participate in the chemical reaction and acts as source or sink for electrons. If the electrode is reactive, it participates in the electrode reaction.

(iii) different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials.

(iv) overvoltage (kinetic barrier), some of the thermodynamically feasible electrochemical processes are so slow kinetically that at lower voltage these do not seem to take place and hence, an extra voltage (or overpotential or overvoltage) is required for them.

Overpotential *(Bubble Potential)*

Some reactions although feasible, are so slow that they do not appear to be occurring. Hence, extra potential called overpotential is applied, which results in evolution of gaseous product (like H_2, O_2) in the form of bubbles.

It can also be defined as the difference between the potential required for the evolution of the gas and its standard reduction potential.

Some Important Examples of Electrolysis

(i) **Electrolysis of molten sodium chloride** It produces sodium metal at the cathode and chlorine gas at the anode. This happens according to the following reactions :

At cathode $Na^+(aq) + e^- \longrightarrow Na(s)$

At anode $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

(ii) **Electrolysis of aqueous solution of sodium chloride** (brine) It is more complicated. Since, the solution is in water, so there are two dissociation reactions producing four different ions.

$$NaCl \longrightarrow Na^+ + Cl^-$$

$$H_2O \longrightarrow H^+ + OH^-$$

At cathode, there are two possible reactions

$$Na^+(aq) + e^- \longrightarrow Na(s); \quad E^\circ_{cell} = -2.71 \text{ V}$$

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g); \quad E^\circ_{cell} = 0.00 \text{ V}$$

The reaction with the higher value of E° is preferred. Thus, the reaction at the cathode during electrolysis is

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g) \quad \text{...(i)}$$

But $H^+(aq)$ is produced by the dissociation of H_2O,

i.e. $H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$ ...(ii)

Therefore, net reaction at the cathode are the sum of Eqs. (i) and (ii)

$$H_2O(l) + e^- \longrightarrow \frac{1}{2}H_2(g) + OH^- \quad \text{...(iii)}$$

At anode, possible oxidation reactions are

$$Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-, E^\circ_{cell} = 1.36 \text{ V}$$

$$OH^- \longrightarrow \frac{1}{2}H_2O + \frac{1}{4}O_2 + e^- \quad \text{...(iv)}$$

or, $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$, $E^\circ_{cell} = 1.23$ V ...(v)

Reaction (v) is the sum of reaction (ii) and reaction (iv). The reaction with the lower value of E° is preferred at the anode. Thus, we expect oxidation of water to take place at the anode. However, due to the oxygen overpotential, liberation of chlorine gas is preferred. Hence,

At cathode

$$H_2O(l) + e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-(aq)$$

At anode $Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-$

Net reaction

$$NaCl(aq) + H_2O(l) \longrightarrow Na^+(aq) + OH^-(aq) + \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$$

(iii) Electrolysis of brine using, Hg as a cathode, then

At cathode $Na^+ + e^- \longrightarrow Na$

$$Na + Hg \longrightarrow Na—Hg$$

$$2Na—Hg + 2H_2O \longrightarrow 2NaOH + Hg + H_2(g)$$

At anode

$$Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-;\ E^\circ_{cell} = 1.36\text{ V}$$

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-;\ E^\circ_{cell} = 1.23\text{ V}$$

The reaction with lower value of E° should be preferred but due to overvoltage of oxygen, Cl_2 gas is discharged at anode.

(iv) During electrolysis of sulphuric acid the following reactions are possible:

At anode

(i) $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-;\ E^\circ_{cell} = +1.23\text{ V}$

(ii) $2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-;\ E^\circ_{cell} = 1.96\text{ V}$

For dilute sulphuric acid, reaction (i) is preferred but at higher concentration of H_2SO_4, reaction (ii) is preferred.

At cathode $H^+ + e^- \longrightarrow \frac{1}{2}H_2(g);\ E^\circ_{cell} = 0.00\text{V}$

TOPIC PRACTICE 3

OBJECTIVE Type Questions

1. The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is .... **NCERT Exemplar**
(a) 1 F (b) 6 F (c) 3 F (d) 2 F

2. An electrolytic cell contains alumina. If we have to obtain 50 g Al by using 105 A of current, the time required is
(a) 1.54 hr (b) 2.15 hr
(c) 1.42 hr (d) 1.32 hr

3. What will be the weight of silver deposited, if 96.5 A of current is passed into aqueous solution of $AgNO_3$ for 100 s?
(a) 1.08 g (b) 10.8 g
(c) 108 g (d) 1080 g

4. 1.5 A current is flowing through a metallic wire. If it flows for 3 hrs, how many electrons would flow through the wire?
(a) 2.05×10^{22} electrons (b) 1.0×10^{23} electrons
(c) 10^{24} electrons (d) 4.5×10^{23} electrons

5. 6 A current with 75% efficiency is passed through a cell for 6 h? ($z = 4 \times 10^{-4}$). The amount of metal deposited will be
(a) 22.4 g (b) 36.0 g (c) 32.4 g (d) 38.8 g

6. Same amount of electricity is passed through the solutions of HCl and $CuSO_4$. If 6.35g of copper is deposited from $CuSO_4$ solution, the amount of hydrogen liberated at STP will be
(a) 0.01 (b) 0.1
(c) 0.001 (d) 1

7. What will happen to pH of brine solution if electrolysed?
(a) pH will decrease (b) pH will increase
(c) pH remains the same (d) pH = 7

8. Which of the following reaction is preferred at anode during the electrolysis of H_2SO_4 at higher concentration?
(a) $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-,\ E^\circ = 1.23\text{ V}$
(b) $2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-,\ E^\circ = 1.96\text{ V}$
(c) Both (a) and (b) (d) None of these

VERY SHORT ANSWER Type Questions

9. How much charge is required for the reduction of 1 mole of Cu^{2+} to Cu? **NCERT**

10. When acidulated water (dil. H_2SO_4) is electrolysed, will the pH of the solution be affected? Justify your answer. **NCERT Exemplar**

SHORT ANSWER Type I Questions

11. (i) Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution:

$$Ag^+(aq) + e^- \longrightarrow Ag(s); \quad E^\circ = +0.80\text{ V}$$

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g); \quad E^\circ = 0.00\text{ V}$$

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?

(ii) Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration? **Delhi 2015**

12. Consider the reaction,

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

What is the quantity of electricity in coulombs, needed to reduce 1 mole of $Cr_2O_7^{2-}$? **NCERT Intext**

13. What is the amount of charge required to carry out the conversion of 1 mole of Al^{3+} ions to Al according to the following reaction,

$$Al^{3+} + 3e^- \longrightarrow Al$$

Or How much charge is required for the reduction of 1 mole of Al^{3+} to Al? **NCERT**

14. If a current of 0.5 A flows through a metallic wire for 2 h, then how many electrons would flow through the wire? **NCERT Intext**

15. How much charge is required for the following reduction: 1 mole of MnO_4^- to Mn^{2+}? **Delhi 2020, NCERT**

16. Calculate the time required to deposit 1.27 g of copper at cathode when a current of 2 A was passed through the solution of $CuSO_4$. (Molar mass of Cu = 63.5 g mol^{-1}, 1 F = 96500 C mol^{-1}) **All India 2015**

SHORT ANSWER Type II Questions

17. How much electricity is required in coulomb for the oxidation of

(i) 1 mole of H_2O to O_2?

(ii) 1 mole of FeO to Fe_2O_3? **NCERT**

18. Chromium metal is electroplated using an acidic solution containing CrO_3 according to the following equation:

$$CrO_3(aq) + 6H^+ + 6e^- \longrightarrow Cr(s) + 3H_2O$$

Calculate how many grams of chromium will be electroplated by 24,000 coulombs. How long will it take to electroplate 1.5 g chromium using 12.5 A current?

[Atomic mass of Cr = 52 g mol^{-1},
1 F = 965000 C mol^{-1}] **All India 2019**

19. (i) The cell in which the following reaction occurs:

$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$,

has $E^\circ_{cell} = 0.236$ V at 298 K. Calculate the standard Gibbs energy of the cell reaction. (Given, 1 F = 96500 C mol^{-1})

(ii) How many electrons flow through a metallic wire, if a current of 0.5 A is passed for 2 h? (given, 1 F = 96500 C mol^{-1}) **All India 2017**

LONG ANSWER Type Questions

20. Three electrolytic cells *A*, *B* and *C* containing solutions of zinc sulphate, silver nitrate and copper sulphate, respectively are connected in series.

A steady current of 1.5 A was passed through them until 1.45 g of silver deposited at the cathode of cell *B*. How long did the current flow? What mass of copper and zinc were deposited in the concerned cells?

(Atomic mass of Ag = 108, Zn = 65.4, Cu = 63.5) **Delhi 2008; NCERT**

21. When a steady current of 2A was passed through two electrolytic cells *A* and *B* containing electrolytes $ZnSO_4$ and $CuSO_4$ connected in series, 2 g of Cu were deposited at the cathode of cell *B*. How long did the current flow? What mass of Zn was deposited at cathode of cell *A*?

[Atomic mass : Cu = 63.5 g mol^{-1},
Zn = 65 g mol^{-1}; 1 F = 96500 C mol^{-1}] **Delhi 2020**

HINTS AND EXPLANATIONS

1. (c) The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is equal to number of electron required to convert Al_2O_3 to Al.

$$Al^{3+}(aq) \xrightarrow{+3e^-} Al(s)$$

Hence, total 3F is required.

2. (c) $Al^{3+} + 3e^- \longrightarrow Al$

Equivalent weight of Al $= \frac{27}{3} = 9$

From Faraday's first law, $w = zit = \frac{E}{96500} it$

$\therefore \quad t = \frac{50 \times 96500}{9 \times 105} = 5105.82\,s = 1.42$ hr

3. (b) $Q = it = 96.5 \times 100 = 9650$ C

96500 C charge deposited weight of Ag = 108 g

9650 C deposited weight of Ag $= \frac{108 \times 9650}{96500} = 10.8$ g

4. (b) Charge on one electron $= 1.6 \times 10^{-19}$ C

As, $Q = it = 1.5 \times 3 \times 3600 = 16200$C

$\therefore$ 16200C charge is on $\frac{1 \times 16200}{1.6 \times 10^{-19}} = 1.0 \times 10^{23}$ electrons

5. (d) $w = zit = 4 \times 10^{-4} \times 6 \times \frac{75}{100} \times 6 \times 3600 = 38.8$ g

6. (b) From Faraday's second law,

$$\frac{w_{H_2}}{w_{Cu}} = \frac{E_{H_2}}{E_{Cu}} \Rightarrow w_{H_2} = \frac{1}{63.5} \times 6.35 = 0.1\text{ g}$$

7. (b) H_2 is liberated at cathode and Cl_2 at anode during the electrolysis of NaCl solution. NaOH is formed so pH will rise.

8. (b) During the electrolysis of H_2SO_4 (dilute)

(i) $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$; $E^\circ_{cell} = 1.23$ V

During the electrolysis of conc. H_2SO_4

(ii) $2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$; $E^\circ_{cell} = 1.96$ V

The reaction with lower value of E° should be preferred but due to overvoltage of O_2, hence reaction (ii) will be preferred.

9. $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

Charge required for the reduction of 1 mole of Cu^{2+}

$= 2F = 2 \times 96500\,C = 193000$ C

10. pH of the solution depends upon the concentration of H^+ ions present in solution. Thus, pH of the solution will not be affected as (H^+) remains constant.

At anode $\quad 2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

At cathode $\quad 4H^+ + 4e^- \longrightarrow 2H_2$

11. (i) Electrolysis of an aqueous solution of AgCl.

$$AgCl(aq) \longrightarrow Ag^+(aq) + Cl^-(aq)$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

On passing electricity, $Ag^+(aq)$ and $H^+(aq)$ move towards the cathode, since, the discharge potential of Ag^+ ion is lower than that of H^+ ions. In the other words, Ag^+ ions have more value of standard reduction potential.

Therefore, Ag^+ ions are discharged in preference to H^+ ions.

At cathode $\quad Ag^+(aq) + e^- \longrightarrow Ag(s)$

At anode $\quad Cl^- - e^- \longrightarrow Cl$

$\quad Cl + Cl \longrightarrow Cl_2(g)$

Hence, reduction of Ag^+ (ion) is feasible at cathode.

(ii) Refer to text on page 65.

12. In the given reaction, one $Cr_2O_7^{2-}$ ion requires 6 electrons for reduction. Therefore, 1 mole of $Cr_2O_7^{2-}$ ions requires 6F, i.e. 6×96500 C= 579000C of electricity for reduction.

13. The number of electrons involved in the reaction is three.

Therefore, the amount of electricity required for one mole of Al^{3+} ions $= 3F$ or $3 \times 96500\,C = 289500$C

14. Here, current $i = 0.5$ A, time $t = 2$ h

Quantity of charge (Q) passed = Current $(i) \times$ Time (t)

$= (0.5\text{ A}) \times (2 \times 60 \times 60\text{ s})$

$= 3600$ A s $= 3600$ C

Again, $\quad Q = ne^-$

where, n = number of electrons, e^- = charge on electron

$\therefore \quad n = \frac{Q}{e^-}$

$= \frac{3600\text{C}}{1.6 \times 10^{-19}\text{C}}$

$= 2250 \times 10^{19}$

Thus, number of electrons $= 2.250 \times 10^{22}$

15. The charge on manganese is +7 in MnO_4^-. The chemical reaction involved is

$$Mn^{7+} + 5e^- \longrightarrow Mn^{2+}$$

Therefore, to convert 1 mole of MnO_4^- to Mn^{2+} ions, 5F of electricity is required. The amount of charge is therefore, $5 \times 96500\,C = 482500$ C.

16. Since, 63.5 g of Cu is deposited by 96500C

$\therefore$ 1.27 g of Cu is deposited by

$= \frac{96500}{63.5} \times 1.27 = 1930$ C

As, $\quad Q = I \times t$ [where, Q=charge, I=current, t= time]

$\Rightarrow \quad t = \frac{Q}{I}$

Here, $\quad I = 2$A, $Q = 1930$ C

$\therefore \quad t = \frac{1930}{2} = 965$ s

17. (i) $H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

$\therefore$ The electricity required for the oxidation of 1 mole of H_2O is 2 F = 2 × 96500 C
$= 193000\ C = 1.93 \times 10^5\ C$

(ii) $FeO \longrightarrow \frac{1}{2}Fe_2O_3$

i.e. $\underset{1\ mol}{Fe^{2+}} \longrightarrow Fe^{3+} + \underset{1F}{e^-}$

$\therefore$ The electricity required is 1 F = 1 × 96500 C
= 96500 C

18. Given Charge (Q) = 24000 C and current (I) = 12.5 A.
Mass of chromium (Cr) deposited = 1.5 g
Molar mass of (Cr) = 52 and 1 F = 96500 C mol^{-1}

$\because$ 6 × 96500 C charge, deposit Cr = 52 g

$\therefore$ 24000 C charge, deposit Cr $= \frac{52 \times 24000}{6 \times 96500} = \frac{1248000}{6 \times 96500}$

Mass of chromium deposited = 2.16 g

Also,

$\because$ Charge $(Q) = i \times t$ (time)

$\therefore$ $t = \frac{Q}{i} = \frac{24000}{12.5} = 1920\ s$

Duration of current = 32 min

19. (i) Refer to solution 28 on page 61.
(ii) Refer to example 1 on page 73.

20. $Ag^+ + \underset{1F}{e^-} \longrightarrow \underset{1mol}{Ag}$

$\because$ 108 g of Ag is deposited by 96500 C

$\therefore$ 1.45 g of Ag will be deposited by $= \frac{96500 \times 1.45}{108}$
= 1295.6 C

$Q = it$ or 1295.6 C = 1.5 A × t

$\therefore$ $t = \frac{1295.6\ C}{1.5} \Rightarrow t = 863.7\ s$

The reaction related to the deposition of copper is

$Cu^{2+} + 2e^- \longrightarrow \underset{63.5\ g}{Cu}$

$\because$ 2 × 96500 C electricity deposits 63.5 g of Cu

$\therefore$ 1295.6 C electricity will deposit
$\frac{63.5 \times 1295.6}{2 \times 96500}$ g of Cu, i.e. 0.426 g of Cu.

The reaction related to the deposition of zinc is

$Zn^{2+} + \underset{2\ \times\ 96500\ C}{2e^-} \longrightarrow \underset{65.4\ g}{Zn}$

$\because$ 2 × 96500 C electricity deposits 65.4 g of Zn.

$\therefore$ 1295.6 C electricity will deposit $\frac{65.4 \times 1295.6}{2 \times 96500}$ g of Zn,

i.e. 0.44 g of Zn.

21. Given, Current, I = 2 A
Two electrolytes $CuSO_4$ and $ZnSO_4$ connected in series

$Cu^{2+} + 2e^- \longrightarrow \underset{(63.5\ g)}{Cu}$

$\therefore$ 2 × 96500 C electricity deposits 63.5 g of Cu

2g of Cu will be deposited by $= \frac{96500 \times 2 \times 2}{63.5} = 6078.74\ C$

$Q = I \times t$

6078.74 C = 2A × t

$t = \frac{6078.74}{2} = 3039.4\ s$

$Zn^{2+} + 2e^- \longrightarrow Zn$

$\therefore$ 2 × 96500 C electricity deposits 65 g Zn.

$\therefore$ 6078.74 C electricity will deposits
$= \frac{65 \times 6078.74}{2 \times 96500}$ g of Zn = 2.05 g of Zn

$\therefore$ 2.05 g of Zn was deposited at cathode of cell A.

|TOPIC 4| Electrochemical Cells in Action

BATTERIES (COMMERCIAL CELLS)

A battery (which contains one or more than one electrochemical cell connected in series) or a cell that we use as a source of electrical energy is basically a galvanic cell, which converts the chemical energy of the redox reaction into electrical energy.

For a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use.

There are mainly two types of batteries:

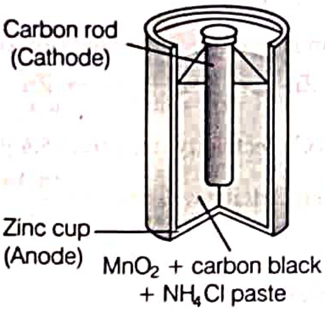
Primary Batteries

A primary battery (non-chargeable battery) is a device in which reactions occur only once and after use (over a period of time), battery becomes dead and cannot be reused. It produces electric current for a period of time and with time when no more chemicals remain available to take part in the reaction, the cell dies. The most familiar examples of this type are Leclanche cell and mercury cell.

1. Leclanche Cell (Dry Cell)

It consists of a zinc container which acts as the anode. The cathode is a carbon (graphite) rod surrounded by a mixture of powdered manganese dioxide and carbon.

The space between the electrodes is filled with moist paste of ammonium chloride and zinc chloride.



Dry cell

The reactions occurring at the cathode and the anode are:

At anode $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

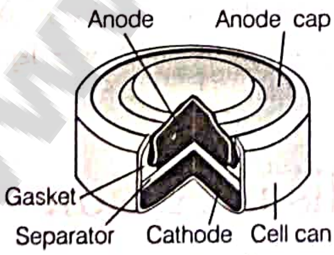
At cathode $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

In the reaction at cathode, manganese is reduced from the +4 oxidation state to the +3 state. NH_3 produced in the reaction forms a complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$. The cell has a potential of about 1.5 V.

Use of Leclanche cell It is commonly used in transistors and clocks.

2. Mercury Cell

It consists of zinc-mercury amalgam as anode. The cathode is a paste of mercuric oxide (HgO) and carbon powder. The electrolyte consists of a mixture of KOH and ZnO.



Mercury cell

The reducing agent is zinc and the oxidising agent is mercury (II) oxide.

The electrode reactions of a mercury cell can be written as:

At anode

$$Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$$

At cathode

$$HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$$

The overall reaction of the cell is written as:

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

The potential of a mercury cell is approximately 1.35 V. It remains constant as in the overall cell reaction no ions are involved in solution whose concentration can change during the life span of the cell. Thus, it lasts longer.

Use of mercury cell It is suitable for low current devices like hearing aids, watches, etc.

Secondary Batteries

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles. Two important secondary batteries — lead storage battery and nickel- cadmium battery are as follows

1. Lead Storage Battery

It consists of a lead anode and a grid of lead packed with lead dioxide as cathode. A 38% solution of sulphuric acid acts as the electrolyte. When the battery is in use (discharging), the cell reactions are:

At anode

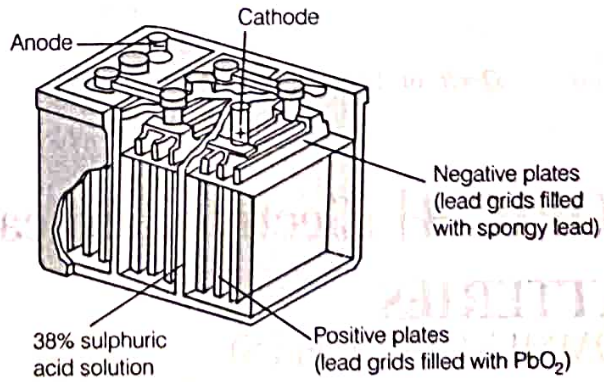
$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

At cathode

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

The overall reaction of the cell is written as:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$



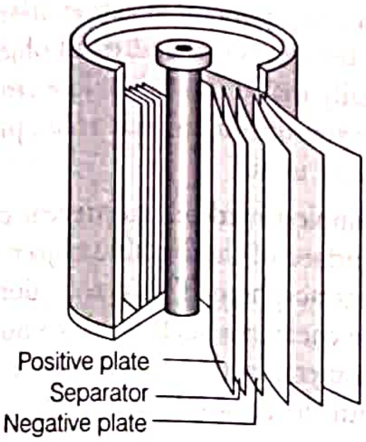
The lead storage battery

During charging, current is passed through the terminals from external source. The reactions are reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively.

Use of Lead storage Battery It is commonly used in automobiles and power inverters.

2. Nickel-Cadmium Battery

It consists of a cadmium anode and metal grid containing NiO_2 as cathode. KOH solution is electrolyte.



A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide

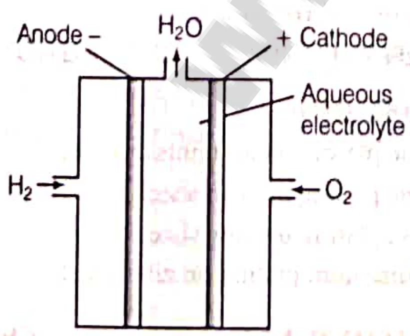
The overall cell reaction of Ni-Cd cell during discharging is

$$Cd(s) + 2Ni(OH)_3(s) \longrightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$$

It has longer life than the lead storage cell but more expensive to manufacture.

FUEL CELL

It is a galvanic cell in which chemical energy from combustion of fuels like hydrogen, methane, methanol, etc., is converted into electrical energy. In this type of galvanic cells, reactants are continuously feed to the electrodes, which react to produce electricity and products thus formed are continuously removed from the electrolyte department. It is highly efficient (70%) method when compared to the efficiency of thermal power plants (40%), that is a major source of pollution.



Fuel cell using H_2 and O_2 produces electricity

One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water. It was used for providing electrical power in Apollo space programme.

The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts.

In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Finely divided platinum or palladium acts as a catalyst.

The electrode reactions for the cell are

At cathode

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

At anode

$$2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$$

The overall reaction of the cell is written as:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

This cell runs as long as the reactants are supplied. There have been tremendous progress in the development of new electrode materials, better catalyst and electrolytes for increasing the efficiency of fuel cells.

These have been used in automobiles on an experimental basis.

CORROSION

It is an electrochemical process in which a metal is oxidised to metal oxide or other salt of the metal by losing electrons to oxygen or other electronegative element and forms a coating on the metal surface. The rusting of iron, tarnishing of silver surface, surface of copper and bronze turning green are some of the examples of corrosion.

Rusting (or corrosion) occurs in the presence of water and air. The place of iron object where rusting takes place, acts as anode. This is the place at which oxidation occurs and iron oxide is formed.

Electrons release at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in the presence of H^+ which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water. This spot behaves as the cathode.

The anode and cathode reactions are:

At anode $2Fe(s) \longrightarrow 2Fe^{2+}(aq) + 4e^-$;

$$E^{\ominus}_{(Fe^{2+}/Fe)} = -0.44\text{ V}$$

At cathode $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$;

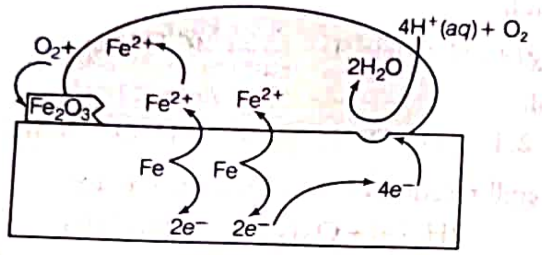
$$E^{\ominus}_{H^+|O_2|H_2O} = 1.23\text{ V}$$

The overall reaction of the cell is written as:

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l);$$
$$E^\ominus_{(cell)} = 1.67\ V$$

The ferrous ions obtained are further oxidised by atmospheric oxygen to ferric ion which comes out as rust in the form of hydrated ferric oxide ($Fe_2O_3.xH_2O$) and with further production of H^+ ions.

e.g., corrosion of iron in atmosphere.



Atmospheric oxidation

$$2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) + 4H^+(aq)$$

Prevention of Corrosion

Prevention of corrosion not only saves money but also helps in preventing accidents such as bridge collapse or failure of a key component. It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. We lose crores of rupees every year on account of corrosion. So, prevention of corrosion is very useful.

One of the simplest methods to prevent corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by applying paint or some chemicals such as bisphenol on the surface of the metal so that the surface does not come in contact with the atmosphere.

The other way is to cover the surface by coating the metal surface with inert metals like zinc, tin, etc. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.

TOPIC PRACTICE 4

OBJECTIVE Type Questions

1. Anode in the Leclanche cell is

(a) zinc container (b) graphite electrode

(c) carbon (d) MnO_2 + C

2. In a lead storage battery **All India 2020**

(a) PbO_2 is reduced to $PbSO_4$ at the cathode.

(b) Pb is oxidised to $PbSO_4$ at the anode.

(c) Both electrodes are immersed in the same aqueous solution of H_2SO_4.

(d) All the above are true.

3. Which is/are rechargable batteries?

(a) Nickel-cadmium (b) Lead-storage

(c) Both (a) and (b) (d) None of these

4. When a lead storage-battery is discharged

(a) SO_2 is evolved

(b) lead is formed

(c) lead sulphate is formed

(d) sulphuric acid is consumed

5. A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as

(a) fuel cell (b) electrolytic cell

(c) dynamo (d) Ni-Cd cell

6. Given the standard electrode potentials,

$E^\circ_{Fe^{2+}/Fe} = -0.44\ V$

and $E^\circ_{H^+/O_2/H_2O} = 1.23\ V$

Calculate the E°_{cell} of the corrosion.

(a) − 0.79 V (b) − 1.67 V

(c) 1.67 V (d) + 0.79 V

7. During the rusting of iron

(a) metal acts as cathode

(b) hydrogen ion acts as anode

(c) formula of rust is $Fe_3O_4.xH_2O$

(d) the overall reaction is

$$2Fe + O_2 + 4H^+ \longrightarrow 2Fe^{2+} + 2H_2O$$

8. Galvanisation is

(a) zinc plating on aluminium sheet

(b) zinc plating on iron sheet

(c) iron plating on zinc sheet

(d) aluminium plating on zinc sheet

VERY SHORT ANSWER Type Questions

9. Why does a dry cell become dead after a long time even if it has not been used?

10. Unlike dry cell, the mercury cell has a constant cell potential throughout its useful life. Why? **NCERT Exemplar**

11. What advantage do the fuel cells have over primary and secondary batteries? **NCERT Exemplar**

12. Suggest two materials other than hydrogen that can be used as fuels in fuel cells. **NCERT Intext**

13. Rusting of iron is quicker in saline water than in ordinary water. Give reason.

14. Why does an alkaline medium inhibit the rusting of iron?

15. Why rusting of iron pipe can be prevented by joining it with a piece of magnesium?

16. Using the $E°$ values of A and B, predict which is better for coating the surface of iron $[E°_{(Fe^{2+}/Fe)} = -0.44]$ to prevent corrosion and why?
$E°_{(A^{2+}/A)} = -2.37$ V; $E°_{(B^{2+}/B)} = 0.14$ V **All India 2016**

SHORT ANSWER Type I Questions

17. Write the name of the cell which is generally used in hearing aids. Write the reactions taking place at the anode and the cathode of this cell. **All India 2017**

18. Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and the cathode of this cell. **All India 2017**

19. Mention the reactions occurring at (i) anode (ii) cathode, during working of a mercury cell. Why does the voltage of a mercury cell remain constant during its operation ?

20. From the given cells: Lead storage cell, Mercury cell, Fuel cell and Dry cell **Delhi 2016**
Answer the following
(i) Which cell is used in hearing aids?
(ii) Which cell was used in Apollo Space Programme?
(iii) Which cell is used in automobiles and inverters?
(iv) Which cell does not have a long life?

21. Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging. **NCERT Intext**

22. The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere. **Delhi 2011**

SHORT ANSWER Type II Questions

23. (i) Calculate the mass of Ag deposited at cathode when a current of 2A was passed through a solution of $AgNO_3$ for 15 min.
(Given : Molar mass of Ag = 108 gmol^{-1}
1F = 96500 C mol^{-1}).
(ii) Define fuel cell. **Delhi 2017**

24. (i) Calculate $\Delta_r G°$ for the reaction,
$$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$$
(Given, $E°_{cell} = +2.71$ V, 1 F = 96500 C mol^{-1})
(ii) Name the type of cell which was used in Apollo space programme for providing electrical power. **Delhi 2014**

LONG ANSWER Type Questions

25. Explain how rusting of iron is envisaged as setting up of an electrochemical cell? **NCERT Intext**

26. (i) Calculate $E°_{cell}$ for the following reaction at 298 K:
$$2Al(s) + 3Cu^{2+}(0.01\text{ M}) \longrightarrow 2Al^{3+}(0.01\text{ M}) + 3Cu(s)$$
Given, $E_{cell} = 1.98$ V
(ii) Using the $E°$ values of A and B, predict which is better for coating the surface of iron $[E°(Fe^{2+}/Fe) = -0.44\text{V}]$ to prevent corrosion and why?
Given : $E°(A^{2+}/A) = -2.37$ V,
$E°(B^{2+}/B) = -0.14$ V **Delhi 2016**

HINTS AND EXPLANATIONS

1. (a) Leclanche cell consists of zinc container which acts as the anode.
2. (d) Refer to page 78 (Lead storage battery).
3. (c) Lead storage battery and nickel cadmium battery are two important rechargable batteries.
4. (c) When lead storage battery is discharged, the following reaction takes place and lead sulphate is formed
$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$
5. (a) In thermal power plants, electricity is produced by using chemical energy of fossil fuels like coal etc.
6. (c) $E^\circ_{cell} = E^\circ_{H^+/O_2/H_2O} - E^\circ_{Fe^{2+}/Fe} = 1.23 - (-0.44)$
$= 1.67$ V
7. (d) During rusting of iron, metal acts as anode, hydrogen ion as cathode. The overall reaction is
$$2Fe + O_2 + 4H^+ \longrightarrow 2Fe^{2+} + 2H_2O$$
Formula of rust is $Fe_2O_3 \cdot xH_2O$.
8. (b) Galvanisation is the process of applying a protective zinc coating to iron or steel.
9. A dry cell becomes dead after a long time, even if it has not been used because the acidic NH_4Cl corrodes the zinc container.
10. The potential of mercury cell (~1.35 V) remains constant. As in the overall cell reaction no ions are involved in solution whose concentration can change during the life span of the cell. Thus, it lasts longer.
11. Primary batteries contain a limited amount of reactants and are discharged when the reactants have been consumed. Secondary batteries can be recharged but it takes a long time. Fuel cell run continuously as long as the reactants are supplied to it and products are removed continuously.
12. Methane (CH_4) and methanol (CH_3OH).
13. Rusting of iron is quicker in saline water than in ordinary water. Salt water helps in flow of current in the miniature cell developed on the iron surface, hence it enhance the process of corrosion.
14. Rusting of iron takes place in the presence of H^+ ions. Alkaline medium neutralise the H^+ ions and thereby inhibits rusting.
15. It is due to cathodic protection in which magnesium metal is oxidised in preference to iron and acts as the anode.
16. Metal A have lower electrode potential than metal B. Hence, when A is connected with iron it protects it from oxidation and prevents corrosion.
17. Mercury cell is suitable for low current devices like hearing aids, watches, etc. For the electrode reactions of a mercury cell. Refer to text on page 78.
18. Leclanche cell is commonly used in transistors. Refer to text on page 78.
19. Refer to text on page 81.
20. (i) Mercury cell
(ii) Fuel cell
(iii) Lead storage cell
(iv) Dry cell
21. Refer to text on page 78.
22. Refer to text on pages 79 and 80.
23. (i) Given, current $(I) = 2$ A
Time $(t) = 15$ min
Quantity of electricity passed will be
$Q = It = 2 \times 15 \times 60 = 1800$ C
Electrolysis of $AgNO_3$
$$Ag^+ + e^- \longrightarrow Ag(s)$$
(Atomic mass of Ag = 108 g mol^{-1})
As, 108 g of Ag has 96500 C
$\therefore$ 1800 C will deposit $= \dfrac{108 \times 1800}{96500}$ g of Ag
$= 2014$ g of Ag
(ii) Refer to text on page 79.
24. (i) For the reaction,
$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s), n = 2$
$E^\circ_{cell} = +2.71$ V, 1F = 96500 C mol^{-1} (given)
$\Delta G^\circ = -nFE^\circ_{cell}$
$= -2 \times 96500 \times 2.71 = -523030$ J mol^{-1}
$= -523.030$ kJ mol^{-1}
(ii) H_2-O_2 fuel cell was used in Apollo space programme for providing electrical power.
25. In corrosion, a metal is oxidised by the loss of electrons to oxygen with the formation of oxides. So, an electrochemical cell is set-up, e.g. rusting of iron
Refer to text on page 79.
26. (i) $2Al(s) + 3Cu^{2+}(0.01M) \longrightarrow 2Al^{3+}(0.01M) + 3Cu(s)$
$E_{cell} = 1.98$ V
Applying Nernst equation for the given cell reaction,
$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$$
$$E^\circ_{cell} = E_{cell} + \frac{0.0591}{n}\log\frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$$
Here, $n = 6$ (n = number of electrons transferred)
$= 1.98 + \dfrac{0.0591}{6}\log\dfrac{(0.01)^2}{(0.01)^3} = 1.98 + \dfrac{0.0591}{6}\log 100$
$= 1.98 + \dfrac{0.0591}{6} \times 2$
[$\because \log 100 = \log 10^2 = 2\log 10 = 2$ as $\log 10 = 1$]
$= 1.9997$ V ≈ 2.0 V
(ii) Refer to solution 16 on page 82.

SUMMARY

- Electrochemistry deals with the relationship between electrical and chemical energy.
- Device which converts chemical energy to electrical energy is called electrochemical cell while that in which electrical energy is used to carry out a non-spontaneous reaction, is called electrolytic cell.
- **Electrochemical or voltaic (galvanic) cells** are of a type that produce electricity as a result of chemical reaction.

  For $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Cu(s) + Zn^{2+}(aq)$,

  cell is $Zn \mid Zn^{2+}(C_1) \| Cu^{2+}(C_2) \mid Cu$

  For $H_2(g) \longrightarrow 2H^+ + 2e^-$, half-cell is $Pt(H_2) \mid H^+(C)$ $\underset{1\text{ atm}}{}$
- **In galvanic cell** oxidation occurs at anode and is a –ve plate, reduction occurs at cathode and is a +ve plate
- Potential difference between the metal and the metal ion in which electrode is dipped, is **electrode potential** (E) in a given state and standard electrode potential ($E°$) in a standard state:

  $E°_{Zn/Zn^{2+}} = E°_{ox}$ (standard oxidation potential of Zn/Zn^{2+})

  $E°_{Cu^{2+}/Cu} = E°_{red}$ (standard reduction potential of Cu^{2+}/Cu)

  $E°_{cell} = E°_{ox} + E°_{red}$. (take $E°$ values according to reaction)

  $E_{cell} = E_{ox} + E_{red}$, $E°_{cell} = E°_R - E°_L$

  $E°_R$ and $E°_L$ are standard reduction potential
- In electrochemical series (ECS), $E°_{red}$ values measured *wrt* (SHE) are arranged in increasing order. Based on ECS, reaction is spontaneous if reducing agent is above oxidising agent.

  Metals lying above hydrogen in ECS will react with dilute acid forming H_2.

  Oxides of Hg and below it in ECS will give metal on heating.
- Nernst equation : $E_{cell} = E°_{cell} - \dfrac{2.303\,RT}{nF}\log K$

  $E_{cell} = E°_{cell} - \dfrac{0.0591}{n}\log K$, where K is reaction quotient

  for $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$; $K = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$ (used also if half-cells are given).
- Electrical work, $\Delta G = -nFE$ in a given state

  $\Delta G° = -nFE°$ in a standard state

  $\Delta G° = -2.303\,RT\log K_{eq}$
- $E°_{cell} = \dfrac{2.303\,RT}{nF}\log K_{eq} = \dfrac{0.0591}{n}\log K_{eq}$ at 298 K
- **Conductors** Substances which allows the electric current to flow through it. The conductors may be metallic or electrolytic.
- The power of an electrolyte to conduct electric current is called **conductance** or **conductivity.**
- Conductance is defined as reverse of resistance, which measures the obstruction in the flow of current while conductivity is reciprocal of resistivity.
- Conductance : ohm^{-1} or S (Siemen)
- Specific conductance : $ohm^{-1}\ cm^{-1}$ or $ohm^{-1}\ m^{-1}$ or $S\ m^{-1}$
- Cell constant : cm^{-1} or m^{-1}
- Specific conductance = conductance × cell constant

  Λ_{eq} = equivalent conductance = $\dfrac{1000 \times \text{specific conductance}}{\text{conc. (normality)}}$

  Λ_m = molar conductance = $\dfrac{1000 \times \text{specific conductance}}{\text{conc. (molarity)}}$

  Λ_{eq} : $ohm^{-1}\ cm^2\ equiv^{-1}$ or $S\ cm^2\ equiv^{-1}$ or $S\ m^2\ equiv^{-1}$

  Λ_m : $ohm^{-1}\ cm^2\ mol^{-1}$ or $S\ cm^2\ mol^{-1}$ or $S\ m^2\ mol^{-1}$
- Debye-Huckel Onsager equation

  $$\Lambda_m = \Lambda_m^\infty - [A + B\Lambda_m^\infty]\sqrt{C}.$$

  A and B are called Debye-Huckel constants.
- Λ_{eq}^∞ and Λ_m^∞ both increase with decrease in concentration (or increase in dilution) and when $C \to 0$, $\Lambda_{eq} = \Lambda_{eq}^\infty$

  $$\Lambda_m = \Lambda_m^\infty$$

  Λ_{eq}^∞ and Λ_m^∞ are values at infinite dilution such that $C \to 0$
- By Kohlrausch's law, $\Lambda_m^\infty = x\lambda_+^\infty + y\lambda_-^\infty$
- **In electrolytic cell** Oxidation occurs at anode but is +ve plate, reduction occurs at cathode but is –ve plate.
- **By Faraday's law**

  First law

  w (amount deposited) $= zit = zC$

  where, z is electrochemical equivalent,

  $$z = \frac{\text{atomic wt.}}{n \times 96500}$$

  i = current (in amp), t = time (in sec.)

  C = Coulombs of electricity, thus 1 F of electricity will deposit 1 g equivalent of metal, i.e., 108 g of Ag, 12 g of Mg and 9 g of Al.
- **Second law**

  $$\frac{\text{wt. of metal } A}{\text{wt. of metal } B} = \frac{\text{eq. wt. of } A}{\text{eq. wt. of } B}$$
- Electrolysis of molten NaCl(l) gives sodium at cathode; electrolysis of *aq*. NaCl solution gives NaOH and H_2 at cathode and Cl_2 at anode.
- Electrolysis of acidified H_2O

  At anode $\quad 2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$

  At cathode $\quad 2H_2O + 2e^- \longrightarrow 2OH^- + H_2$
- Electrolysis of $CuSO_4(aq)$

  with inert electrode

  $$Cu^{2+} + H_2O \longrightarrow Cu + 2H^+ + \frac{1}{2}O_2$$

  - Principle used in **electroplating**

  with copper electrode

  $$\underset{\text{Anode}}{Cu(s)} \longrightarrow \underset{\text{Cathode}}{Cu(s)}$$
- The corrosion of metals, such as the rusting of iron, is an electrochemical phenomenon.
- Batteries, which consist of one or more electrochemical cells, are used widely as self-contained power sources, e.g. dry cell, lead storage battery etc.

CHAPTER PRACTICE

MULTIPLE CHOICE Type Questions

The following questions are multiple choice questions. Choose the most appropriate answer :

1 An electrochemical cell can behave like an electrolytic cell when ....

(a) $E_{cell} = 0$ (b) $E_{cell} > E_{ext}$
(c) $E_{ext} > E_{cell}$ (d) $E_{cell} = E_{ext}$

2 Which metal cannot replace H_2 from hydrochloride acid?

(a) Zn (b) Cu (c) Mg (d) Al

3 In the given reaction,

$$2Cu^+(aq) \rightleftharpoons Cu^{2+}(aq) + Cu(s)$$

$E^\circ_{Cu^+/Cu} = 0.6$ V and $E^\circ_{Cu^{2+}/Cu} = 0.41$ V

Find out the equilibrium constant.

(a) 2.76×10^2 (b) 2.76×10^4
(c) 2.76×10^6 (d) 2.76×10^8

4 Select the correct statement for $\Lambda_m = \Lambda^\circ_m - AC^{1/2}$.

(a) This equation is for weak electrolyte
(b) Intercept is equal to Λ_m
(c) Slope is 'A'
(d) Value of A depends on the charges of cation and anion

5 While charging the lead storage battery ....

(a) $PbSO_4$ at anode is reduced to Pb
(b) $PbSO_4$ at cathode is reduced to Pb
(c) $PbSO_4$ at cathode is oxidised to Pb
(d) $PbSO_4$ at anode is oxidised to PbO_2

6 The mathematical expression for molar conductivity is

(a) $\Lambda_m = \dfrac{M}{\kappa \times 1000}$ (b) $\Lambda_m = \dfrac{\kappa \times 1000}{M}$
(c) $\Lambda_m = \dfrac{\kappa}{M \times 1000}$ (d) $\Lambda_m = \dfrac{M \times 1000}{\kappa}$

7 What are the units of molar conductivity, Λ_m?

(a) $\Omega^{-1}\ m^2\ mol^{-1}$ (b) $S\,cm^2 mol^{-1}$
(c) Both (a) and (b) (d) None of these

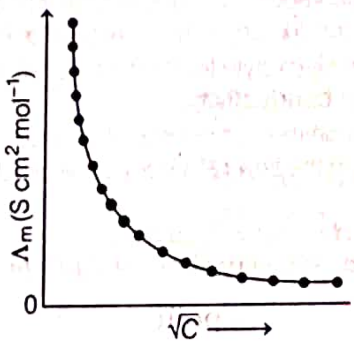
8 Conductivity of 0.00241M acetic acid is $7.896 \times 10^{-5} S\ cm^{-1}$. Calculate its molar conductivity in this solution?

(a) 2.41×10^{-2} (b) 7.896×10^{-6}
(c) 32.76 (d) 14.76

9 How does molar conductivity varies with concentration for strong as well as weak electrolytes?

(a) Molar conductivity increases with decrease in concentration
(b) Total volume (V) of solution containing one mole of electrolyte increases
(c) Both (a) and (b)
(d) None of the above

Or Given graphical representation of variation of conductivity with concentration for which electrolytes?



(a) Weak (b) Strong
(c) Very strong (d) None of these

CASE BASED Questions

Case I

Molar conductivity of a solution is the conductance of solution containing one mole of electrolyte, kept between two electrodes having unit length between them and large cross sectional area so as to contain the electrolyte. In other words, molar conductivity is the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. It is denoted by Λ_m.

Case II

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity. A galvanic cell directly converts chemical energy into electricity and is highly efficient.

Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called **fuel cells**.

One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water. The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions.

In the question that follow Assertion and Reason are given. Reason is purported to the explaination for Assertion. Study carefully and then mark your answers, according to the codes given below.

Marks your answer as :

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

10 **Assertion** Fuel cell is a galvanic cell.

Reason It convert the energy of combustion fuel into electrical energy.

11 **Assertion** Efficiency of fuel cell is 70% as compared to thermal plants.

Reason Thermal plants have 40% efficiency.

12 **Assertion** Electrolytes used in fuel cells.

Reason Conc. KOH (*aq*) solution can not be used as electrolyte.

13 **Assertion** H_2O_2 fuel cell has many advantages.

Reason It causes pollution.

Or **Assertion** Fuel cell has no such importance of uses.

Reason They used in automobiles.

ASSERTION AND REASON

■ **Directions** (Q. Nos. 14-21) *In the following questions. an Assertion (A) is followed by a corresponding Reason (R) Use the following keys to choose the appropriate answer.*

(a) Both (A) and (R) are correct, (R) is the correct explanation of (A).

(b) Both (A) and (R) are correct, (R) is not the correct explanation of (A).

(c) (A) is correct; (R) is incorrect.

(d) (A) is incorrect; (R) is correct.

14 **Assertion** (A) Conductivity always increases with decrease in concentration for strong and weak electrolytes.

Reason (R) Number of ions per unit volume decreases on dilution.

15 **Assertion** (A) Conductivity of pure water is 3.5×10^{-5} S m^{-1}.

Reason (R) High amounts of hydrogen and hydroxyl ions are present in water.

16 **Assertion** Pure water conducts electricity.

Reason Pure water exists in unionised form.

17 **Assertion** (A) Solid NaCl does not conduct electricity.

Reason (R) Solid NaCl has no free ions.

18 **Assertion** (A) Mercury cells give a constant voltage throughout its life.

Reason (R) Electrolyte KOH is not involved in the reaction.

19 **Assertion** (A) 96500 C charge is required for the reduction of one mole of silver ions.

Reason (R) The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction.

20 **Assertion** (A) H_2—O_2 fuel cell gives a constant voltage throughout its life.

Reason (R) In this fuel cell, H_2 reacts with OH^- ions yet the overall concentration of OH^- ions does not change.

21 **Assertion** (A) Electrolysis of an aqueous solution of KI gives I_2 at the anode but that of KF gives O_2 at the anode not F_2.

Reason (R) I^- ions have much lower oxidation potential than water while F^- ions have much higher oxidation potential than water.

VERY SHORT ANSWER Type Questions

22 Write the cell representation for the galvanic cell used for measuring standard electrode potential of iron having, $E^\circ_{Fe^{2+}/Fe} = -0.44$ V.

23 In a galvanic cell, what is the polarity of anode?

24 Write the Nernst equation to calculate the cell potential of $Mg(s)\,|Mg^{2+}(aq)\,||Ag^+|Ag$.

25 When does an electrochemical cell behaves like an electrolytic cell?

26 Can absolute electrode potential of an electrode be measured?

27 What does the negative sign in the expression $E^\circ_{Zn^{2+}/Zn} = -0.76$ V mean?

28 List the factors on which molar conductivity of ionic solution depends.

29 List the factors on which conductivity of electrolyte depends.

30 The specific conductivity of a saturated solution of silver chloride is 2.30×10^{-6} S cm^{-1} at 25°C. Calculate the solubility of silver chloride at 25°C. Λ^∞ for Ag^+ and Cl^- ions are 61.9 and 76.3 S cm^2 mol^{-1} respectively.

31 From the values of a Faraday (96500 C) and Avogadro number (6.023×10^{23}), calculate the coulomb charge on an electron.

32 How will the pH of brine (*aq* NaCl solution) be affected when it is electrolysed?

33 What is a primary cell? Give one example.

34 What features of a cell enables practical use of battery?

35 Mention the uses of mercury cell.

36 What is the advantage of nickel-cadmium cell over lead-storage battery?

37 List the advantages of using H_2-O_2 fuel cell over ordinary cell.

38 Write the Nernst equation for single electrode potential.

39 What is the efficiency of a fuel cell? What is the use of a fuel cell?

40 Suggest a metal that can be used for cathodic protection of iron against rusting.

41 Write the relation between cell potential and equilibrium constant.

42 Why does a cell stops working after sometime?

SHORT ANSWER Type I Questions

43 Write the Nernst equation and emf of the following cell at 298 K.
$Fe(s)|Fe^{2+}(0.001M)||H^+(1M)|H_2(g)\,(1\text{ bar})|Pt$

44 The potential for the cell below is found to be 0.25 V.
$Pt(s)\,|H_2(g)|H^+(aq), (1\text{ mol/L})||\,Cu^{2+}(aq, C\text{ mol/L})|\,Cu(s)$
What is the value of C?

45 A solution of $MgSO_4$ is electrolysed for 20 min with a current of 1.5 A. What mass of magnesium is deposited at the cathode?

46 (i) What are metallic conductors?
(ii) What is molar conductivity?

47 The emf of a cell corresponding to the reaction
$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(0.1\text{ M}) + H_2(g, 1\text{atm})$ is 0.28 V at 25°C.
Write the half-cell reaction and calculate the pH of the solution at the hydrogen electrode.
$E^\circ_{Zn^{2+}/Zn} = -\,0.76$ V, $E^\circ_{H^+/H_2} = 0$

48 Find the equilibrium constant for the reaction,
$Cu^{2+} + In^{2+} \rightleftharpoons Cu^+ + In^{3+}$
Given that, $E_{Cu^{2+}/Cu^+} = 0.15$ V,
$E^\circ_{In^{2+}/In^+} = -\,0.4$ V, $E^\circ_{In^{3+}/In} = 0.42$ V

49 A current of 3.7 A is passed for 6 h between nickel electrodes in 0.5 L of a 20 M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis?

50 What is a nickel-cadmium cell? State its one merit and one demerit over lead storage cell. Write the overall reaction that occurs during discharging of this cell.

51 Give an example of a fuel cell and write the cathode and anode reactions for it.

52 How is galvanisation different from cathodic protection of iron?

53 A lead-storage cell can act both as galvanic and electrolytic cells. Explain.

54 State and explain three methods of prevention of rusting of iron.

55 Calculate the emf for the given cell at 25°C.
$Cr|Cr^{3+}$ (0.1 M)|| Fe^{2+} (0.01 M)|Fe
[Given, $E^\circ_{Cr^{3+}/Cr} = -0.74$ V, $E^\circ(Fe^{2+}/Fe) = -0.44$ V]

56 A strip of nickel metal is placed in a 1 molar solution of $Ni(NO_3)_2$ and a strip of silver metal is placed in a one molar solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter.

(i) Write the balanced equations for the overall reaction occurring in the cell

(ii) Calculate the cell potential, E, at 25° C for the cell, if the initial concentration of $Ni(NO_3)_2$ is 0.100 molar and the initial concentration of $AgNO_3$ is 1.00 molar.
[$E^\circ_{Ni^{2+}/Ni} = -0.25$ V, $E^\circ_{Ag^+/Ag} = 0.80$ V, $\log 10^{-1} = -1$]

57 Which of the following solutions has larger molar conductance?

(i) 0.08 M solution having conductivity equal to $2.0 \times 10^{-2} \Omega^{-1} cm^{-1}$.

(ii) 0.10 M solution having resistivity equal to 58 Ωcm .

58 Conductivity of two electrolyte solutions A and B each having a concentration of 0.1 M are $8.5 \times 10^{-2} S\ cm^{-1}$ and 4.1×10^{-4} S cm^{-1} respectively. Which of the two offers less resistance to the flow of current ?

59 The Λ°_m values for NaCl and KCl are 126.5 and 149.9 $\Omega^{-1} cm^2 mol^{-1}$ respectively. The ionic conductance of Na^+ at infinite dilution is 50.1 $\Omega^{-1}cm^2 mol^{-1}$. Calculate the ionic conductance at infinite dilution for potassium ion (K^+).

60 Calculate the degree of dissociation of acetic acid at 298 K, given that

$\Lambda^\circ_{m\ (CH_3COOH)} = 11.7$ S cm^2 mol^{-1}

$\Lambda^\circ_{m\ (CH_3COO^-)} = 40.9$ S cm^2 mol^{-1}

$\Lambda^\circ_{m\ (H^+)} = 349.1$ S cm^2 mol^{-1}

61 In the electrolysis of sulphuric acid, there are two possible anodic reactions.

$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$, $E^\circ = 1.23$ V

$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$, $E^\circ = 1.96$ V

Which reaction occurs at anode and why?

62 Explain why electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode? Write overall reaction.
Given, $E^\circ_{Na^+/Na} = -2.71$ V, $E^\circ_{H_2O/H_2} = -0.83$ V,
$E^\circ_{Cl_2/Cl^-} = +1.36$ V, $E^\circ_{H^+/H_2/H_2O} = +1.23$ V

SHORT ANSWER Type II Questions

63 Calculate the standard cell potential at 25°C for the electrochemical cells, Zn | Zn^2 || reference half-cell and reference half-cell ||Cu^{2+}|Cu, where the reference half-cell is,

(i) SHE (ii) Ag/AgCl electrode.

64 Calculate the standard electrode potential of Ni^{2+}|Ni electrode if emf of the cell,
Ni(s)|Ni^{2+}(0.01 M)||Cu^{2+}(0.1 M)|Cu(s) is 0.059 V.
[Given, $E^\circ_{Cu^{2+}/Cu} = +0.34$ V]

65 How many molecules of chlorine should be deposited from molten sodium chloride in one minute by a current of 300 mA?

66 Calculate the standard free energy change taking place in H_2-O_2 fuel cell in which the following reactions occur.

(i) $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$; $E^\circ = 1.229$ V

(ii) $2H_2 \longrightarrow 4H^+ + 4e^-$; $E^\circ = 0.000$ V

67 Degree of dissociation of pure water is 1.9×10^{-9}. Molar ionic conductances of H^+ ions and OH^- ions at infinite dilution are 200 S cm^2 mol^{-1} and 350 S $cm^2 mol^{-1}$ respectively. What is the molar conductance of water?

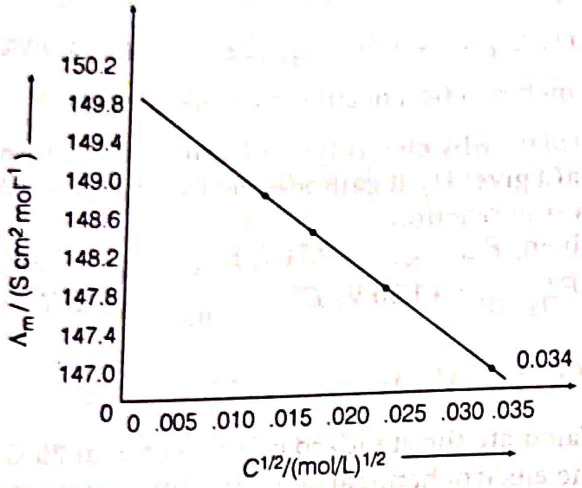
68 Consider the following cell reaction;

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l); E^\circ = 1.67 \text{ V}$$

At $[Fe^{2+}] = 10^{-3}$ M, $p(O_2) = 0.1$ atm and pH = 3.

What is the cell potential at 25°C?

69 The molar conductivity (λ_m) of KCl solutions, at different concentration at 298 K, is plotted as shown in the figure given below:



Determine the value of λ_m° and A for KCl.

70 Give the half-cell and net cell reactions in the following batteries.

(i) Mercury cell
(ii) Lead storage battery
(iii) Lithium-manganese dioxide cell

71 Calculate the potential for half-cell containing 0.10 M $K_2Cr_2O_7(aq)$, 0.20 M $Cr^{3+}(aq)$ and 1.0×10^{-4} M $H^+(aq)$. The half-cell reaction is

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

and the standard electrode potential is given as $E^\circ = 1.33$ V.

72 One half-cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. The other half-cell consists of a zinc electrode in a 0.10 M solution of $Zn(NO_3)_2$. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver nitrate solution.
[Given, $E^\circ_{Zn^{2+}/Zn} = -0.763$ V, $E^\circ_{Ag^+/Ag} = +0.80$ V]

73 Electric current is passed through two cells A and B in series. Cell A contains aqueous solution of Ag_2SO_4 and platinum electrodes. Cell B contains aqueous solution of $CuSO_4$ and copper electrodes. The current is passed till 1.6 g of oxygen is liberated at the anode in cell A. Calculate the quantities of copper and silver deposited at the cathode of the two cells.
[Atomic mass O = 16, Cu = 63.5, Ag = 108]

74 (i) Calculate the strength of the current required to deposit 1.2 g of magnesium from molten $MgCl_2$ in 1 h.
[1 F = 96500 C mol^{-1}, atomic mass of Mg = 24.0]

(ii) An electric current of 0.15 A is passed through 500 mL of 0.15 M copper sulphate solution. How much time is required to deposit all the copper?

75 In the process of electrolysis of CrO_3, the following reaction occurs.

$$CrO_3(aq) + 6H^+ + 6e^- \longrightarrow Cr(s) + 3H_2O$$

Calculate

(i) amount of chromium deposited when 24,000 C of charge passed.
(ii) time required to deposit 1.5 g chromium using 12.5 A current. (Atomic mass of (Cr = 52))

LONG ANSWER Type Questions

76 Discuss the products obtained in electrolysis of aqueous solution of brine.

77 Calculate the equilibrium constant for the reaction

$$2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$$

The standard reduction potential in acidic condition is 0.78V and 0.54 V, respectively, for Fe^{3+}/Fe^{2+} and I_3^-/I couples.

78 Iron may be protected from rusting by coating with zinc or tin. By referring to the data given below, explain why zinc protects iron more effectively than tin?

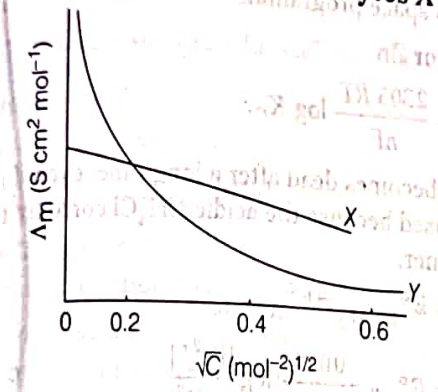
$Zn^{2+} + 2e^- \longrightarrow Zn$; $E^\circ = -0.76$ V
$Fe^{2+} + 2e^- \longrightarrow Fe$; $E^\circ = -0.44$ V
$Sn^{2+} + 2e^- \longrightarrow Sn$; $E^\circ = -0.14$ V

79 (i) Why hydrogen is considered as a fuel resource for future?
(ii) How can we generate energy from hydrogen fuel?
(iii) Why do we need to reduce our usage of carbonacious fuels?

80 (i) Write the chemistry of discharging the Leclanche cell, highlighting all the materials that are involved during cell reactions. State its use.
(ii) What is the difference between primary and secondary cells? Differentiate using their applications also.
(iii) Prevention of corrosion is of prime importance. Comment.

81 Write the Nernst equation and emf of the following cells at 298 K.
(i) $Sn(s)|Sn^{2+}(0.050M)||H^+(0.020M)|H_2(g, 1bar)|Pt(s)$
(ii) $Pt(s)|Br_2(l)|Br^-(0.010M)||H^+(0.030M)|H_2(s,1bar)|Pt(s)$

82 The following curve is obtained when molar conductivity, Λ_m is plotted against the square root of concentration, $C^{1/2}$ along y and x-axis respectively for the two electrolytes X and Y.



(i) What can you say about the nature of these two electrolytes?
(ii) Account for the increase in Λ_m for the electrolytes X and Y with dilution.
(iii) Determine Λ_m^∞ for these electrolytes.

83 (i) How much time is required for 1.5 g Ag to deposit when 1.50 A current is passed through an electrolytic cell containing $AgNO_3$ solution with inert electrodes?
(ii) Write the reactions taking place at anode and cathode in case of
(a) Pt electrodes.
(b) Ag electrodes.

84 (i) Two electrolytic cells containing silver nitrate solution and dilute sulphuric acid were connected in a series. A steady current of 2.5 A was passed through them till 1.078 g of silver was deposited (Ag = 107.8 g/mol)
(a) How much electricity was consumed?
(b) What is the weight of oxygen gas liberated during the reaction?
(ii) How many grams of Hg will be produced by electrolysing 1.0 M $Hg(NO_3)_2$ solution with a current of 2.00 A for 3 hours?
$[Hg(NO_3)_2 = 200.6 \text{ g/mol}]$

ANSWERS

1 (c) 2 (b) 3 (c) 4 (d) 5 (a)

6 (b) The mathematical expression for molar conductivity is given as,

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

where, Λ_m = molar conductivity of solution
κ = conductivity of solution
M = molarity of the solution

7 (c) The units of molar conductivity Λ_m are $\Omega^{-1} m^2 mol^{-1}$ or $S\ cm^2\ mol^{-1}$.

8 (c) Given, $\kappa = 7.896 \times 10^{-5}\ S\ cm^{-1}$

Molarity $(M) = 0.00241$ M

$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa \times 1000}{M}$$

$$= \frac{7.896 \times 10^{-5}\ S\ cm^{-1} \times 1000}{0.00241\ M}$$

$$\Lambda_m = 32.76\ S\ cm^2\ mol^{-1}$$

9 (c) Molar conductivity increases with decrease in concentration. This is because, the total volume (V) of solution containing one mole of electrolyte increases.

Or (a) The graphical representation of variation of molar conductivity with concentration for weak electrolytes is given as.

10 (a) Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called **fuel cells.** Both (A) and (R) are correct and (R) is the correct explanation of (A).

11 (b) They have an efficiency of 70% as compared to thermal plants whose efficiency is 40%.
Both (A) and (R) are correct but (R) is not correct explanation of (A).

12 (c) Electrolytes are used in fuel cells and conc. aqueous solution of KOH is used as electrolyte. Only (A) is correct.

13 (c) (i) It does not cause pollution
(ii) It has high efficiency of 60-70%. Only (A) is true.

Or (d) They have been used in automobiles on an experimental basis. Only (R) is correct.

14 (d) Conductivity always decreases with decrease in concentration for weak and strong electrolytes. This is explained by the decrease in the number of ions per unit volume that carry current in solution on dilution. Thus, (A) is incorrect but (R) is correct.

15 (c) Pure water has small amounts of hydrogen and hydroxyl ions ($\sim 10^{-7}$ M) due to which it has very low conductivity (3.5×10^{-5} S m^{-1}). Thus, (A) is correct but (R) is incorrect.

16 (d) Pure water do not conduct electricity because it is unionised. Thus, (A) is incorrect but (R) is correct.

17 (a) Solid NaCl does not conduct electricity due to the absence of free ions.
Thus, both (A) and (R) are correct and (R) is the correct explanation of (A).

18 (c) Mercury cell gives the constant voltage throughout its life because the overall reaction does not involve any ion in the solution, concentration of which changes during its whole life. Thus, (A) is correct but (R) is incorrect.

19 (a) Both (A) and (R) are correct and (R) is the correct explanation of (A).

20 (a) Both (A) and (R) are correct and (R) is the correct explanation of (A).

21 (c) (A) is correct but (R) is incorrect. The correct (R) is I^- ions have much higher oxidation potential than water while F^- ions have much lower oxidation potential than water.

22 $Fe|Fe^{2+}||H^+|H_2(g)|Pt(s)$

23 Negative

24 $E_{cell} = E°_{cell} - \frac{0.059}{n} \log \frac{[Mg^{2+}]}{[Ag^+]^2}$

25 $E_{ext} > E_{cell}$

26 No.

27 Negative $E°$ means that the redox couple is stronger reducing agent than H^+/H_2.

28 Inter-ionic attraction, polarity of a solvent, viscosity, temperature and concentration.

29 Charge on ions, size of the ions in which they dissociate and concentration of ions.

30 [Ans $s = 1.67 \times 10^{-5}$ mol L^{-1}]

31 Charge $= N_A \times 1.6021 \times 10^{-19} = 96500$ C mol^{-1}

32 When aqueous NaCl solution is electrolysed, H_2 is liberated at cathode, Cl_2 at anode and NaOH is formed in the solution. Hence, pH of solution will rise.

33 A primary battery or cell is a device in which reactions occurs only once and after use (over a period of time), battery becomes dead and can not be reused. e.g. mercury cell.

34 For a battery to be of practical use it should be resonably light, compact and its voltage should not vary appreciably during its use.

35 **Uses of mercury cell** It is suitable for low current devices like hearing aids, watches, etc.

36 Nickel-cadmium battery has longer life than the lead storage cell.

37 $H_2 - O_2$ fuel cell run continuously as long as the reactions are supplied to it and products are removed continuously.

38 For $M^{n+}(aq) + ne^- \longrightarrow M(s)$

$$E_{M^{n+}/M} = E°_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

39 Fuel cell is highly efficiency (70%) method when compared to the efficiency of thermal power plants (40%) that is a major source of pollution. Fuel cell have been used in automobiles on an experimental basis. H_2 - O_2 fuel cell was used for providing electrical power in Apollo space programme.

40 Cr, Sn or Zn.

41 $E°_{cell} = \frac{2.303\, RT}{nF} \log K_C$.

42 A cell becomes dead after a long time, even if it has not been used because the acidic NH_4Cl corrodes the zinc container.

43 $E_{cell} = E°_{H^+/H_2} - E°_{Fe^{2+}/Fe}$

$$E_{cell} = E°_{cell} - \frac{0.0591}{n} \log \frac{[Fe^{2+}]}{[H^+]^2}$$

44 [Ans $C = 8.89 \times 10^{-4}$ mol^{-1}]
Refer to text on page 55 [Nernst equation].

45 Refer to example 1 on page 73.

46 (i) Refer to text on page 63.
(ii) Refer to text on page 64.

47 Refer to solution 18 on page 60. **[Ans. pH = 8.6]**

48 [Ans $K = 10^{10}$]

49 [Ans $M = 1.172$ M]

50 Refer to text on page 79.

51 Refer to text on page 79.

52 Refer to text on page 80.

53 Refer to text on pages 78.

54 Refer to text on page 80.

55 Refer to solution 25 on page 61.

56 (i) $Ni(s) + 2Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$
(ii) $E_{cell} = 1.0795$V
Refer to solution 19 on page 60.

57 (i) $\Lambda_m = 250\ \Omega^{-1} cm^2 mol^{-1}$
(ii) $\Lambda_m = 172.4\ \Omega^{-1}\ cm^2 mol^{-1}$
Thus, solution (i) has larger molar conductance

58 $\kappa \propto \frac{1}{R}$
Hence, B will offer greater resistance

59 $\lambda°_{K^+} = 73.5\ \Omega^{-1}\ cm^2\ mol^{-1}$

60 Refer to solution 23 on page 70.

61 Refer to text on page 74.

62 Refer to text on page 73 and 74.

63 [Ans (i) 0.76 V, 0.34 V (ii) 0.98 V, 0.12 V]

64 [Ans 0.31 V]

65 [Ans 5.616×10^{19} molecules]

66 [Ans -474.4 kJ]

67 [Ans 1.045×10^{-6} S cm^2 mol^{-1}]

68 [Ans 1.57 V]

69 Refer to solution 23 on pages 70.

70 (i) Refer to text on page 78.
(ii) Refer to text on page 78.
(iii) At anode : $Li(s) \longrightarrow Li^+ + e^-$
At cathode : $MnO_2(s) + Li^+ + e^- \longrightarrow LiMnO_2(s)$

71 [Ans $E_{cell} = 0.78V$]

72 [Ans $= 1.24 \times 10^{-2}$ M]

73 [Ans Ag = 21.6 g, Cu = 6.35 g]

74 (i) [Hint $Q = i \times t$]
(ii) Refer to solution 16 on page 76.

75 (i) Refer to solution 18 on page 77.
(ii) Refer to solution 16 on page 76.

76 Refer to text on page 74.

77 [Hint $E^\circ_{cell} = \frac{0.0591}{n} \log K$] [Ans $K_{eq} = 10^8$]

78 Refer to solution 16 on page 82.

79 Refer to text on page 79.

80 (i) Refer to text on page 77 and 78.
(ii) Refer to text on pages 77 and 78.
(iii) Refer to text on page 80.

81 Refer to solution 22 on page 61.

82 Refer to text on pages 65 and 66.

83 (i) Refer to text on page 52.
(ii) Refer to text on page 52 and 53.

84 (i) (a) Refer to solution 20 on page 77 [Ans 965C]
(b) Refer to solution 20 on page 77 [Ans 0.16g]
(ii) $Hg^{2+} + 2e^- \longrightarrow Hg$
Quantity of electricity $= i.t$
$= 2\text{ A} \times 3 \times 60 \times 60 = 21600\text{ C}$
2×96500 C of electricity produce mercury = 1 mol
21600 C of electricity will produce mercury
$= \frac{1}{2 \times 96500} \times 21600 = 0112$ mol

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03

CHEMICAL KINETICS

For any chemical reaction, **thermodynamics** tells about the feasibility of a reaction (for any physical-chemical reaction, $\Delta G < 0$, at constant temperature and pressure), **chemical equilibrium** tells about the extent to which a reaction will proceed and **chemical kinetics** tells about the rate at which a chemical reaction proceeds and the factors which control this rate.

The word kinetics is derived from the Greek word '*kinesis*' meaning movement. **Chemical kinetics** is the branch of chemistry which deals with the study of the chemical reactions with respect to the reaction rates the factors affecting the rate of reactions and the mechanism by which the reactions proceed.

Consider two reactions, i.e. rusting of iron nail and combustion of propane. Here, the latter reaction take few seconds for its completion while rusting of iron may take few hours, days or even weeks for its initiation. So, there are factors which affect the rate of chemical reactions. The study of these factors and rates is known as chemical kinetics.

CHAPTER CHECKLIST

- Rate of Chemical Reaction, Rate Expression and Rate Constant
- Order and Molecularity of a Chemical Equation
- Integrated Rate Equations
- Temperature Dependence of the Rate of a Reaction

|TOPIC 1|
Rate of Chemical Reaction, Rate Expression and Rate Constant

CHEMICAL REACTIONS

When one or more substances undergo a change which results in the formation of a new product, it is called chemical reaction. On the basis of their speeds, chemical reactions are of three types which are as follow :

(i) **Very fast reactions** Some reactions (such as ionic reactions) occur very fast, e.g. precipitation of $AgCl$ from $AgNO_3$ and $NaCl$.

(ii) **Very slow reactions** Some reactions are very slow, e.g. rusting of iron in the presence of air and moisture.

(iii) **Moderately slow reactions** Some reactions occur at moderate speed, e.g. inversion of cane sugar and hydrolysis of starch.

Note Reactions involving ionic species are very fast reactions. Ionic reactions generally occur in 10^{-12} to 10^{-16}s.

On the basis of number of steps, chemical reactions are of two types as follows :

(i) **Elementary Reactions** A balanced chemical equation does not give a true picture of how a reaction takes place. It is very rare that the reaction gets completed in one step.
The reactions taking place in one step are called the **elementary reactions.**

(ii) **Complex Reactions** When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called **complex reactions.** Each step in a complex reaction is called elementary step of a reaction.
Complex reactions may be consecutive reactions (e.g. oxidation of ethane to CO_2 and H_2O passes through a series of intermediate steps in which alcohol, aldehyde and acid are formed), reverse reactions and side reactions (e.g. nitration of phenol yields *o*-nitrophenol and *p*-nitrophenol).

RATE OF A CHEMICAL REACTION

Rate of chemical reaction means the speed with which the reaction takes place. The speed of a vehicle is expressed in terms of distance travelled per unit time, in the same way, the speed or the rate of a chemical reaction can be defined as the change in concentration of reactants or products per unit time. It can be expressed in terms of

(i) the rate of decrease in concentration of any one of the reactants, or

(ii) the rate of increase in concentration of any one of the products.

Consider a simple hypothetical reaction, assuming that the volume of the system remains constant such that one mole of the reactant R produces one mole of the product P,

$$R \longrightarrow P$$

If $[R]_1$ and $[P]_1$ are the concentrations of reactant, R and product, P respectively at time t_1 and $[R]_2$ and $[P]_2$ are the concentrations at time t_2, then

$$\Delta t = t_2 - t_1$$

$$\Delta R = [R]_2 - [R]_1 \quad \text{or} \quad \Delta P = [P]_2 - [P]_1$$

(Here, the square brackets are used to express molar concentration.)

Rate of disappearance of R

$$= \frac{\text{Decrease in concentration of } R}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t} \quad \dots(i)$$

Rate of appearance of P

$$= \frac{\text{Increase in concentration of } P}{\text{Time taken}} = +\frac{\Delta[P]}{\Delta t} \quad \dots(ii)$$

Since, $\Delta[R]$ is a negative quantity (as concentration of reactant is decreasing), it is multiplied by -1 to make the rate of the reaction a positive quantity as rate is always a positive quantity. e.g.

For the reaction,

$$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$$

Rate may be expressed as :

$$\text{Rate} = -\frac{\Delta[PCl_5]}{\Delta t} = \frac{\Delta[PCl_3]}{\Delta t} = \frac{\Delta[Cl_2]}{\Delta t}$$

Note Symbol Δ is used for larger change and symbol '*d*' is used for smaller change.

Units of rate of reaction Unit of rate of reaction is concentration time^{-1}. If concentration is in mol L^{-1} and time is in second, then the units of rate of reaction will be mol $L^{-1}s^{-1}$. However, in gaseous reactions when the concentration of gases is in terms of their partial pressures, the unit of rate of expressed their reaction will be atm s^{-1}.

Average and Instantaneous Rate of Reaction

If the rate of appearance of products or disappearance of reactants comprises over a long interval of time then it is expressed as **average rate of reaction,** r_{av}.

$$\therefore \quad r_{av} = -\frac{\Delta[R]}{\Delta t} \quad \dots(i)$$

$$= +\frac{\Delta[P]}{\Delta t} \quad \dots(ii)$$

Eqs. (i) and (ii) represent the average rate of a reaction (r_{av}), which depends upon the change in concentration of reactants or products and the time taken for that change to occur.

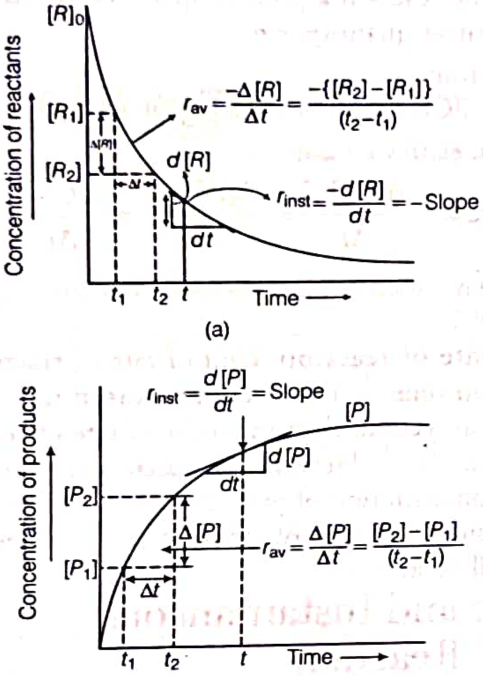
The concentration of reactants goes on decreasing with time, therefore, the rate of a reaction does not remain constant throughout the reaction process. Thus, cannot be determined simply by dividing the total change in concentration by the time taken. In other words, rate of a reaction may be expressed at a particular moment of time. Such a reaction rate is called **instantaneous rate of reaction** (r_{inst}). It is expressed as

$$\therefore \quad r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

As $\Delta t \rightarrow 0$, Instantaneous rate = Average rate

Experimental Determination of Rate of a Reaction

Rate of a reaction can be determined from the slope of the graph between the concentration of any of the reactants or products and time as given below:



Determination of instantaneous and average rate of a reaction

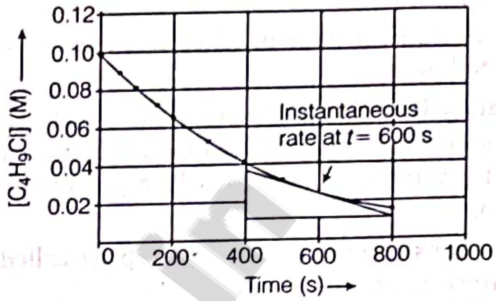
e.g. Consider the following reaction,

$$C_4H_9Cl + H_2O \longrightarrow C_4H_9OH + HCl$$

during different intervals of time.

t/s	$[C_4H_9Cl]$/mol L^{-1}
0	0.100
50	0.0905
100	0.0820
150	0.0741
200	0.0671
300	0.0549
400	0.0439
700	0.0210
800	0.017

Its instantaneous rate can be find out by graphical method.



Instantaneous rate of hydrolysis of butyl chloride (C_4H_9Cl)

Determination of instantaneous rate graphically is done by drawing a tangent at time t on either of the curves for concentration of R and P *vs* time t and calculating its slope (figure). If we plot a graph of concentration of butyl chloride as a function of time and if, we draw a tangent that touches the curve at $t = 600\,s$, then the slope of this tangent gives the instantaneous rate. In the above example, at $t = 600$ s,

$$r_{inst} = -\frac{d[R]}{dt} = -\left(\frac{0.0165 - 0.037}{(800-400)s}\right) \text{mol L}^{-1}$$

$$= 5.12 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

Similarly,

at $t = 250$ s, $r_{inst} = 1.22 \times 10^{-4}$ mol $L^{-1}s^{-1}$

$t = 350$ s, $r_{inst} = 1.0 \times 10^{-4}$ mol $L^{-1}s^{-1}$

$t = 450$ s, $r_{inst} = 6.4 \times 10^{-5}$ mol $L^{-1}s^{-1}$

EXAMPLE |1| For the reaction, $R \longrightarrow P$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 min. Calculate the average rate of reaction using units of time both in minutes and seconds. **NCERT Intext**

> Average rate of reaction = Rate of change of $[R]$ or $[P]$
> $= \frac{\text{Change in concentration of } [R] \text{ or } [P]}{\text{Time taken}}$

Sol. For the reaction, $R \longrightarrow P$

Average rate of reaction

$$= \frac{\text{Change in concentration of reactant/product}}{\text{Time taken}}$$

$$= -\frac{\Delta[R]}{\Delta t} = -\frac{\{[R_2]-[R_1]\}}{t_2 - t_1} = -\frac{(0.02 - 0.03)\text{ M}}{25\text{ min}}$$

$$= \frac{0.01\text{ M}}{25\text{ min}} = 4 \times 10^{-4} \text{ mol L}^{-1}\text{min}^{-1}$$

Converting unit of time in seconds

$$\frac{4 \times 10^{-4}}{60} \text{mol L}^{-1}\text{s}^{-1} = 6.66 \times 10^{-6} \text{ mol L}^{-1}\text{ s}^{-1}$$

Mathematical Expression for Rate of Reaction

(i) If stoichiometric coefficients of the reactants and products are same, then the rate of reaction will be same whether it is expressed in terms of decrease in the concentration of reactants or increase in the concentration of products.

e.g. $\underset{1\text{ mol}}{PCl_5} \longrightarrow \underset{1\text{ mol}}{PCl_3} + \underset{1\text{ mol}}{Cl_2}$

Rate of reaction for such reaction,

$$= -\frac{\Delta[PCl_5]}{\Delta t} = +\frac{\Delta[PCl_3]}{\Delta t} = +\frac{\Delta[Cl_2]}{\Delta t}$$

Similarly, we can take example of

$$Hg(l) + Cl_2(g) \longrightarrow HgCl_2(s)$$

$$\text{Rate of reaction} = -\frac{\Delta[Hg]}{\Delta t} = -\frac{\Delta[Cl_2]}{\Delta t} = +\frac{\Delta[HgCl_2]}{\Delta t}$$

(ii) If the stoichiometric coefficients of reactants and products in the balanced equation are not same or not equal to one, then to get identical value of the rate of reaction in terms of any reactant or product, the rates are divided by their respective stoichiometric coefficients.

e.g. $\underset{2\text{ mol}}{2N_2O_5} \longrightarrow \underset{4\text{ mol}}{4NO_2} + \underset{1\text{ mol}}{O_2}$

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = +\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = +\frac{\Delta[O_2]}{\Delta t}$$

Similarly, for the reaction of decomposition of HI

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = +\frac{\Delta[H_2]}{\Delta t} = +\frac{\Delta[I_2]}{\Delta t}$$

For a more complex reaction,

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

$$\text{Rate of reaction} = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t}$$

$$= -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

EXAMPLE |2| The decomposition of N_2O_5 in CCl_4 at 318 K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N_2O_5 is 2.33 mol L^{-1} and after 184 minutes, it is reduced to 2.08 mol L^{-1}. The reaction takes place according to the equation

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of NO_2 during this period? **NCERT Intext**

Sol. $\text{Average Rate} = \frac{1}{2}\left\{-\frac{\Delta[N_2O_5]}{\Delta t}\right\}$

$$= -\frac{1}{2}\left[\frac{(2.08 - 2.33)\text{ mol L}^{-1}}{184\text{ min}}\right]$$

$$= 6.79 \times 10^{-4}\text{ mol L}^{-1}/\text{min}$$

$$= (6.79 \times 10^{-4}\text{ mol L}^{-1}\text{ min}^{-1}) \times (60\text{min}/1\text{h})$$

$$= 4.07 \times 10^{-2}\text{ mol L}^{-1}/\text{h}$$

$$= 6.79 \times 10^{-4}\text{ mol L}^{-1} \times 1\text{ min}/60\text{s}$$

$$= 1.13 \times 10^{-5}\text{ mol L}^{-1}\text{s}^{-1}$$

According the given equation,

$$\text{Rate} = \frac{1}{4}\left\{\frac{\Delta[NO_2]}{\Delta t}\right\}$$

$$\frac{\Delta[NO_2]}{\Delta t} = 6.79 \times 10^{-4} \times 4\text{ mol L}^{-1}\text{ min}^{-1}$$

$$= 2.72 \times 10^{-3}\text{ mol L}^{-1}\text{ min}^{-1}$$

EXAMPLE |3| For the reaction, $2A \longrightarrow$ products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 min. Calculate the rate during the interval. **NCERT Intext**

Sol. Rate of reaction = Rate of disappearance of A

$$= -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = -\frac{1}{2}\frac{(0.4 - 0.5)\text{ mol L}^{-1}}{10\text{ min}}$$

$$= 0.005\text{ mol L}^{-1}\text{min}^{-1}$$

FACTORS INFLUENCING RATE OF A REACTION

Rate of a chemical reaction depends upon the experimental conditions like concentration of one or more reactants (pressure in case of gases), temperature, catalyst and surface area of the reactants.

(i) **Concentration of reactants** Reactions occur with greater speed when concentration of the reactants is high. Conversely, reaction rate decreases as the concentrations of the reactants decrease.

(ii) **Temperature** It also influences the rate of reaction. Reactions occur with greater speed at higher temperature. Speed of a reaction nearly doubles on 10°C rise in temperature.

(iii) **Catalyst** A catalyst alters the speed of reaction. It helps to attain the equilibrium quickly. It participates in the reaction without being consumed.

(iv) **Surface area of the reactants** Smaller the particle size, greater the surface area and faster is the reaction. So, powdered form of catalyst is better catalyst.

(v) **Nature of the reactants and the products** Rates of reactions are influenced by the nature of reactants and products.
The reactivity of a substance depends on the ease with which the specific bonds are broken or formed.
e.g. The oxidation of nitric oxide to nitrogen dioxide takes place considerably faster while oxidation of CO to CO_2 takes place slowly.

(vi) **Presence of light** Some reactions do not takes place in the dark rather they require light for their initiations.

e.g. $$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

Such reactions are called "photochemical reactions".
Reaction rate normally becomes faster in presence of light. Light gives the necessary activation energy for starting the reaction.

RATE EXPRESSION AND RATE CONSTANT

Rate of a chemical reaction at a given temperature may depend on the concentration of reactants and products. The representation of rate of reaction in terms of concentration of the reactants is called the **rate law, rate equation** or **rate expression.**

Consider a general reaction,

$$aA + bB \longrightarrow cC + dD$$

where, a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for the above reaction is

$$\text{Rate} \propto [A]^x [B]^y$$

where, exponents x and y are determined experimentally and may or may not be equal to the stoichiometric coefficients (a and b) of the reactants. Above equation can also be written as:

$$\text{Rate} = k[A]^x [B]^y$$

$$-\frac{d[R]}{dt} = k[A]^x[B]^y$$

This form of equation is known as **differential rate equation**, where k is the proportionality constant called **rate constant**. With the help of above equation, rate law and rate constant can be described.

Rate Law

It is the expression in which the **reaction rate** is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

Rate law for a chemical reaction cannot be decided from the balanced chemical equation, i.e. theoretically. It has to be determined experimentally.

e.g. $$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

We can measure the rate of this reaction as a function of initial concentrations either by keeping the concentration of one of the reactants constant and changing the concentration of the second reactant or by changing the concentrations of both the reactants.

e.g. If concentration of NO is doubled and that of O_2 is kept constant, then the initial rate increases by a factor of four.

This indicates that the rate depends upon the square of the concentration of NO. When concentration of NO is kept constant and concentration of O_2 is doubled, the initial rate also gets doubled indicating that rate depends on the concentration of O_2 to the first power.

Hence, the rate equation for this reaction will be

$$\text{Rate} = k[NO]^2[O_2]$$

The differential form of this rate expression is

$$\frac{-d[R]}{dt} = k[NO]^2[O_2]$$

In this reaction, the exponents of the concentration terms are same as their stoichiometric coefficients. Some other examples are given below:

(i) $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$

$\text{Rate} = k[CHCl_3][Cl_2]^{1/2}$

(ii) $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

$\text{Rate} = k[CH_3COOC_2H_5]\,[H_2O]^0$

In these reactions, the exponents of the concentration terms are not same as their stoichiometric coefficients. Hence, rate law for any reaction cannot be predicted by merely looking at the balanced chemical equations, i.e. theoretically but must be determined experimentally. We will discuss these exponents in next topic.

Rate Constant (Specific Reaction Rate)

From the rate equation, when concentration of all the reactants is unity, then

$$\text{Rate} = k$$

where, k is called the rate constant.

Hence, it is defined as the **rate of chemical reaction** when concentration of each reactant is unity. The rate constant is also called the specific rate of reaction.

Characteristics of Rate Constant

(i) Rate constant is a measure of the rate of reaction. Greater is the value of the rate constant, faster is the reaction.

(ii) Each reaction has a definite value of the rate constant at a particular temperature and its value for the same reaction changes with change in temperature.

(iii) Its value does not depend upon the concentrations of the reactants.

(iv) The unit of rate constant depends upon the order of reaction.

EXAMPLE |4| The following results have been obtained during the kinetic studies of the reaction, $2A + B \longrightarrow C + D$. **NCERT**

Exp.	$[A]$ / mol L^{-1}	$[B]$ / mol L^{-1}	Initial rate of formation of $[D]$ / mol L^{-1} min^{-1}
1.	0.1	0.1	6.0×10^{-3}
2.	0.3	0.2	7.2×10^{-2}
3.	0.3	0.4	2.88×10^{-1}
4.	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

Sol. Rate law may be expressed as

$$\text{Rate} = k\,[A]^x[B]^y$$

$$(\text{Rate})_1 = 6.0 \times 10^{-3} = k\,(0.1)^x(0.1)^y \quad \text{...(i)}$$

$$(\text{Rate})_2 = 7.2 \times 10^{-2} = k\,(0.3)^x(0.2)^y \quad \text{...(ii)}$$

$$(\text{Rate})_3 = 2.88 \times 10^{-1} = k\,(0.3)^x(0.4)^y \quad \text{...(iii)}$$

$$(\text{Rate})_4 = 2.40 \times 10^{-2} = k\,(0.4)^x(0.1)^y \quad \text{...(iv)}$$

$$\frac{(\text{Rate})_1}{(\text{Rate})_4} = \frac{6.0 \times 10^{-3}}{2.40 \times 10^{-2}} = \frac{k\,(0.1)^x(0.1)^y}{k\,(0.4)^x(0.1)^y}$$

or $\quad \frac{1}{4} = \frac{(0.1)^x}{(0.4)^x} = \left(\frac{1}{4}\right)^x$

$\therefore \quad x = 1$

$$\frac{(\text{Rate})_2}{(\text{Rate})_3} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{k\,(0.3)^x\,(0.2)^y}{k\,(0.3)^x(0.4)^y}$$

or $\quad \frac{1}{4} = \frac{(0.2)^y}{(0.4)^y} = \left(\frac{1}{2}\right)^y$

$\therefore \quad y = 2$

Now, rate law expression is given by

$$\text{Rate} = k\,[A]\,[B]^2$$

Rate constant, k can be determined by placing the values of A, B and rate of formation of D. By taking the values from any experiment, say experiment 2.

$$\text{Rate} = k\,[A]\,[B]^2$$

$$k = \frac{\text{Rate}}{[A]\,[B]^2} = \frac{7.2 \times 10^{-2}\,\text{mol L}^{-1}\,\text{min}^{-1}}{(0.3\,\text{mol L}^{-1})(0.2\,\text{mol L}^{-1})^2}$$

or $\quad k = 6.0\ \text{mol}^{-2}\ \text{L}^2\text{min}^{-1}$

TOPIC PRACTICE 1

OBJECTIVE Type Questions

1. Rate of which of the following reactions can be determined easily?
(a) Rusting of iron in the presence of air and moisture
(b) Hydrolysis of starch
(c) Reaction of silver nitrate with sodium chloride
(d) All of the above

2. Which of the following expressions is correct for the rate of reaction given below?

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

NCERT Exemplar

(a) $\frac{\Delta[Br^-]}{\Delta t} = 5\frac{\Delta[H^+]}{\Delta t}$ (b) $\frac{\Delta[Br^-]}{\Delta t} = \frac{6}{5}\frac{\Delta[H^+]}{\Delta t}$

(c) $\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$ (d) $\frac{\Delta[Br^-]}{\Delta t} = 6\frac{\Delta[H^+]}{\Delta t}$

3. Contact process is used in the formation of sulphur trioxide,

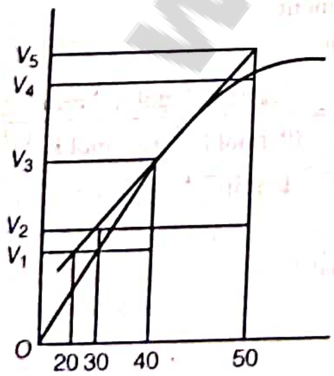
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The rate of reaction can be expressed as $\frac{-\Delta[O_2]}{\Delta t} = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}.

Then rate of disappearance of $[SO_2]$ will be

(a) 50.0×10^{-5} mol L^{-1} s^{-1}
(b) 3.75×10^{-4} mol L^{-1} s^{-1}
(c) 2.5×10^{-4} mol L^{-1} s^{-1}
(d) 4.12×10^{-4} mol L^{-1} s^{-1}

4. A graph of volume of hydrogen released *vs* time for the reaction between zinc and dil. HCl is given in figure. On the basis of this, mark the correct option. **NCERT Exemplar**



(a) Average rate upto 40 s is $\frac{V_3 - V_2}{40}$

(b) Average rate upto 40 s is $\frac{V_3 - V_2}{40 - 30}$

(c) Average rate upto 40 s is $\frac{V_3}{40}$

(d) Average rate upto 40 s is $\frac{V_3 - V_1}{40 - 20}$

5. In a reaction, $2x \rightarrow y$, the concentration of x decreases from 3.0 M to 1.5 M in 4 min. The rate of the reaction is

(a) 0.187 M min^{-1} (b) 1.87 M min^{-1}
(c) 3.75×10^{-1}M min^{-1} (d) 0.75 M min^{-1}

6. Rate law for the reaction $A + 2B \longrightarrow C$ is found to be

$$\text{Rate} = k[A][B]$$

Concentration of reactant '*B*' is doubled, keeping the concentration of '*A*' constant, the value of rate constant will be.......... . **NCERT Exemplar**

(a) the same (b) doubled
(c) quadrupled (d) halved

7. The factors affecting the rate of a reaction are
I. temperature
II. pressure
III. concentration of reactant or product
IV. catalyst

Choose the correct option from the alternatives given below.
(a) I, II and III (b) I, III and IV
(c) II, III and IV (d) All of these

8. During a chemical reaction with increase in temperature, rate of a reaction
(a) decreases (b) increases
(c) remains constant (d) show irregular trends

VERY SHORT ANSWER Type Questions

9. For the reaction

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g),$$

the rate of formation of $NO_2(g)$ is 2.8×10^{-3} Ms^{-1}. Calculate the rate of disappearance of $N_2O_5(g)$. **CBSE 2018**

10. What is the rate of disappearance of hydrogen in the following reaction?

$$3H_2 + N_2 \longrightarrow 2NH_3$$

11. The rate for the formation of C, for the reaction given below, is 2.2×10^{-3} mol L^{-1} min^{-1}.

$$2A + B \longrightarrow C$$

What is the value of $-\frac{d[A]}{dt}$?

12. Why does the rate of any reaction generally decreases during the course of the reaction? **NCERT Exemplar**

13. How is the rate law different from law of mass action?

14. What is the rate for the reaction given below?

$$Cl_2(g) + 2NO(g) \longrightarrow 2NOCl(g)$$

SHORT ANSWER Type I Questions

15. How can average and instantaneous rates of a reaction can be determined from the plot of concentration *versus* time ?

16. Mention the factors that affect the rate of chemical reaction. **NCERT**

17. How can you determine the rate law of the following reaction? **NCERT Exemplar**

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

18. For a reaction the rate law expression is represented as follows: **CBSE SQP 2021**

$$\text{Rate} = k[A][B]^{1/2}$$

(i) Interpret whether the reaction is elementary or complex. Give reason to support your answer.

(ii) Write the units of rate constant for this reaction, if concentration of A and B is expressed in moles/L.

19. The following results have been obtained during the kinetic studies of the reaction:

$$P + 2Q \rightarrow R + 2S$$

Exp.	Initial P (mol/L)	Initial Q (mol/L)	Initial rate of formation of R (M min^{-1})
1	0.10	0.10	3.0×10^{-4}
2	0.30	0.30	9.0×10^{-4}
3	0.10	0.30	3.0×10^{-4}
4	0.20	0.40	6.0×10^{-4}

Determine the rate law expression for the reaction. **CBSE SQP 2021**

SHORT ANSWER Type II Questions

20. For the reaction, $2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$

The following data were collected. All the measurements were taken at 263 K. **CBSE SQP 2021**

Exp. No.	Initial [NO] (M)	Initial $[Cl_2]$ (M)	Initial rate of disappearance of Cl_2 (M/min)
1.	0.15	0.15	0.60
2.	0.15	0.30	1.20
3.	0.30	0.15	2.40
4.	0.25	0.25	?

(i) Write the expression for rate law.

(ii) Calculate the value of rate constant and specify its units.

(iii) What is the initial rate of disappearance of Cl_2 in experiment 4?

HINTS AND EXPLANATIONS

1. (*b*) Rate of only those chemical reactions can be determined easily which occurs at moderate speed, e.g. hydrolysis of starch, inversion of cane sugar etc.

2. (*c*) Given, chemical reaction is

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

Rate law expression for the above equation can be written as

$$-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = \frac{-1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{+1}{3}\frac{\Delta[Br_2]}{\Delta t}$$

$$\Rightarrow \frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$$

3. $$\frac{-\Delta[SO_2]}{\Delta t} = 2\left(-\frac{\Delta[O_2]}{\Delta t}\right)$$

$$\therefore \frac{-\Delta[SO_2]}{\Delta t} = 2 \times 2.5 \times 10^{-4} \text{ mol L}^{-1}\text{ s}^{-1}$$

$$= 5.0 \times 10^{-4} \text{ mol L}^{-1}\text{ s}^{-1}$$

$$= 50.0 \times 10^{-5} \text{ mol L}^{-1}\text{ s}^{-1}.$$

4. (*c*) $Zn + \text{Dil. } HCl \longrightarrow ZnCl_2 + H_2\uparrow$

Average rate of reaction

$$= \frac{\text{Change in concentration of } H_2}{\text{Change in time}} = \frac{V_3 - 0}{40 - 0} = \frac{V_3}{40}$$

5. (a) Rate of reaction $= -\frac{1}{2}\frac{d[x]}{dt} = -\frac{1}{2}\frac{[1.5-3.0]}{4}$

$$= \frac{1.5}{8} = 0.1875 \text{ M min}^{-1}$$

6. (b) Rate law can be written as

$$\text{Rate} = k[A][B]$$

$$R_2 = k[A][2B] = 2R_1$$

Therefore; as concentration of B is doubled keeping the concentration of A constant rate of reaction gets doubled.

7. (d) The factors affecting the rate of a reaction are temperature, pressure, concentration of reactant or product and catalyst.

8. (b) Rate of a reaction increases with increase in temperature.

9. (b) For the reaction, $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

overall rate of reaction is

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = +\frac{d[O_2]}{dt}$$

Given, $\frac{d[NO_2]}{dt} = 2.8 \times 10^{-3}\ \text{Ms}^{-1}$

$$-\frac{d[N_2O_5]}{dt} = ?$$

$$\therefore \quad -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt}$$

Putting the given values in the above equation, we get

$$\frac{-d[N_2O_5]}{dt} = \frac{1}{4} \times 2 \times 2.8 \times 10^{-3}\ \text{Ms}^{-1}$$

$$= 1.4 \times 10^{-3}\ \text{Ms}^{-1}$$

10. Rate of disappearance of hydrogen $= -\frac{1}{3}\frac{d[H_2]}{dt}$

11. $2A + B \longrightarrow C$

Rate of reaction $= -\frac{1}{2}\frac{d[A]}{dt} = +\frac{d[C]}{dt}$

$$\Rightarrow \quad -\frac{d[A]}{dt} = \frac{2d[C]}{dt} = 2 \times 2.2 \times 10^{-3}$$

$$= 4.4 \times 10^{-3} \text{ mol L}^{-1}$$

12. The rate of a reaction depends on the concentration of the reactants. As the reaction proceeds to forward direction, concentration of reactant decreases and that of product increases.

So, the rate of reaction generally decreases during the course of reaction.

13. Rate law states that the rate of reaction depends upon the concentration terms of reaction that is observed experimentally. While the law of mass action is simply based upon the stoichiometry of the equation.

14. Rate $= k[Cl_2][NO]^2$

15. [Hints $r_{av} = -\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$;

$r_{inst} = -\frac{d[R]}{dt}$ (negative slope)

$= \frac{d[P]}{dt}$ (positive slope)]

Refer to the text on page 94.

16. Refer to the text on page 96.

[Hints Concentration, surface area, nature of reactants, temperature, catalyst etc. are the factor that affect the rate of reaction.]

17. Refer to text on pages 96.

[Hint Rate $= k[NO]^2[O_2]$]

18. (i) For an elementary reaction, order of reaction must be equal to the molecularity but molecularity should be integral.

For the given rate law, order of reaction comes out to cannot be $\frac{3}{2}[1+\frac{1}{2}]$. As molecularity be fractional.

Therefore, order is not equal to molecularity. Hence, the given rate law do not belong to an elementary reaction.

(ii) Unit of rate constant are $\text{mol}^{-1/2}\ \text{L}^{1/2}\text{s}^{-1}$.

19. For reaction, $P + 2Q \longrightarrow R + 2S$,

Let the rate law expression be rate $= k[P]^X[Q]^Y$

For experiment 1,

Rate 1 $= 3.0 \times 10^{-4} = k(0.10)^x(0.10)^y$ ...(i)

For experiment 2,

Rate 2 $= 9.0 \times 10^{-4} = k(0.30)^x(0.30)^y$ ...(ii)

For experiment 3,

Rate 3 $= 3.0 \times 10^{-4} = k(0.10)^x(0.30)^y$ ...(iii)

From Eqs. (i) and (iii),

$$\frac{\text{Rate}(1)}{\text{Rate}(3)} = \left(\frac{1}{3}\right)^y \Rightarrow 1 = \left(\frac{1}{3}\right)^y$$

So, $y = 0$, and $\frac{\text{Rate}(2)}{\text{Rate}(3)} = (3)^x \Rightarrow 3 = (3)^x$

So, $x = 1$

$\therefore$ Rate law $= k[P]$

20. (i) The rate law for the reaction

Rate $= k[NO]^2[Cl_2]$ (Refer example 4 on page 133)

(ii) Rate constant can be calculated by substituting the value of rate, $[NO]$ and $[Cl_2]$ for any of the experiments.

$$k = \frac{\text{Rate}}{[NO]^2[Cl_2]} = \frac{0.60}{(0.15)^2(0.15)} = \frac{0.60}{0.00338}$$

$$= 177.51 \text{ mol}^{-2}\text{L}^2\text{min}^{-1}$$

(iii) Let initial rate of disappearance of Cl_2 in experiment 4 is r_4.

$$\therefore \quad r_4 = k[NO]^2[Cl_2] = 177.51 \times (0.25)^2(0.25)$$

$$= 2.78 \text{ M/min}$$

|TOPIC 2|

Order and Molecularity of a Chemical Reaction

ORDER OF A REACTION

The sum of the exponents of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

For a general reaction,

$$aA + bB \longrightarrow cC + dD \quad \text{Rate} = k[A]^x[B]^y$$

Here, x and y, calculated experimentally, indicate how sensitive the rate is to the change in concentrations of A and B. Sum of these exponents, i.e. $x + y$ gives the overall order of a reaction whereas, x and y represent the order with respect to the reactants A and B, respectively.

Order of a reaction can be 0, 1, 2, 3 and even a fraction.

A zero order reaction means that the rate of reaction is independent of the concentration of reactants and the reaction is extremely fast.

For instance, if rate of any reaction is expressed as:

$$\text{Rate} = k[A]^{1/2}[B]^{3/2}$$

Then, order $= x + y = \frac{1}{2} + \frac{3}{2} = 2$

Hence, reaction is said to be of second order.

EXAMPLE |1| For a reaction, $P \longrightarrow Q$, the rate becomes 8 times when concentration of P is doubled. What is the order of the reaction?

Sol. Let Rate, $r = k[P]^n$ ...(i)

$8r = k[2P]^n$ ...(ii)

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{8r}{r} = \frac{k[2P]^n}{k[P]^n}$$

or $[2]^3 = [2]^n$ or $n = 3$

Therefore, order of the reaction is 3.

Units of Rate Constant

The units of rate constants of different orders are different. This can be easily illustrated below:

For a general reaction,

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = k[A]^x[B]^y$$

where, $x + y = n =$ order of the reaction

$$k = \frac{\text{Rate}}{[A]^x[B]^y}$$

$$= \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n}$$

$$= (\text{concentration})^{1-n}\ \text{time}^{-1}$$

(where, $[A] = [B]$)

Considering SI units of concentration, mol L^{-1} and time s, the unit of $k = (\text{mol}\,L^{-1})^{1-n}\,s^{-1}$. Thus, the units of k for different order of reaction are given below:

For zero order ($n = 0$) reaction,

$$\text{Unit of } k = \frac{\text{mol } L^{-1}}{s} \times \frac{1}{(\text{mol } L^{-1})^0} = \text{mol } L^{-1}s^{-1}$$

For first order ($n = 1$) reaction,

$$\text{Unit of } k = \frac{\text{mol } L^{-1}}{s} \times \frac{1}{(\text{mol } L^{-1})^1} = s^{-1}$$

For second order ($n = 2$) reaction,

$$\text{Unit of } k = \frac{\text{mol } L^{-1}}{s} \times \frac{1}{(\text{mol } L^{-1})^2} = \text{mol}^{-1} L\, s^{-1}$$

For nth order reaction,

$$\text{Unit of } k = \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n}$$

$$k = \frac{\text{mol } L^{-1}}{s} \times \frac{1}{(\text{mol } L^{-1})^n}$$

$$= \frac{1}{s} \times \frac{1}{(\text{mol } L^{-1})^{n-1}} = (\text{mol } L^{-1})^{1-n}s^{-1}$$

Note Rate constants of gaseous reactions are expressed in terms of partial pressure instead of concentration.

Summary : Units of rate constants

Reaction	Reaction in solutions	Gaseous reactions
Zero order	mol $L^{-1}s^{-1}$	atm s^{-1}
First order	s^{-1}	s^{-1}
Second order	$\text{mol}^{-1}L\ s^{-1}$	$\text{atm}^{-1}\ s^{-1}$
nth order	$(\text{mol } L^{-1})^{1-n}s^{-1}$	$(\text{atm})^{1-n}\ s^{-1}$

EXAMPLE |2| From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constant. NCERT

(i) $3NO(g) \longrightarrow N_2O(g)$, Rate $= k[NO]^2$

(ii) $H_2O_2(aq) + 3I^-(aq) + 2H^+ \longrightarrow 2H_2O(l) + I_3^-$,

Rate $= k[H_2O_2][I^-]$

(iii) $CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$,

Rate $= k[CH_3CHO]^{3/2}$

(iv) $C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$,

Rate $= k[C_2H_5Cl]$

Sol. (i) Rate $= k[NO]^2$,

Order of reaction = 2

Unit (dimension) of rate constant,

$$k = \frac{\text{Rate}}{[NO]^2} = \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^2} = \text{mol}^{-1}\text{L s}^{-1}$$

(ii) Rate $= k[H_2O_2][I^-]$

Order of reaction = 1 + 1 = 2

$$\text{Dimension of } k = \frac{\text{Rate}}{[H_2O_2][I^-]}$$

$$= \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})(\text{mol L}^{-1})} = \text{mol}^{-1}\text{L s}^{-1}$$

(iii) Rate $= k[CH_3CHO]^{3/2}$

Order of reaction $= \frac{3}{2}$

$$\text{Dimension of } k = \frac{\text{Rate}}{[CH_3CHO]^{3/2}} = \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^{3/2}}$$

$$= \text{mol}^{-1/2}\text{L}^{1/2}\text{s}^{-1}$$

(iv) Rate $= k[C_2H_5Cl]$ Order of reaction = 1

$$\text{Dimension of } k = \frac{\text{Rate}}{[C_2H_5Cl]} = \frac{\text{mol L}^{-1}\text{s}^{-1}}{\text{mol L}^{-1}} = \text{s}^{-1}$$

MOLECULARITY OF A REACTION

Molecularity is an another property of a reaction, which helps in understanding its mechanism. The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of the reaction. e.g. If a reaction involves the decomposition of only a single species, the molecularity is one and it is called unimolecular reaction.

For e.g. in case of decomposition of NH_4NO_2 and O_2F_2, the molecularity is 1.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$
$$O_2F_2 \longrightarrow O_2 + F_2$$

The decomposition of HI is a bimolecular reaction as it involves the collision of two molecules.

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

The reaction between NO and O_2 is a trimolecular reaction as collision of three molecules results into the product.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Reactions with molecularity greater than three (trimolecular) are rare as probability of more than three molecules colliding simultaneously to form product(s) is very low.

Note Molecularity has no meaning for complex reactions as these reactions are supposed to take place in a sequence of a number of steps. It can be determined only for the elementary reactions.

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow KCl + 3Fe_2(SO_4)_3 + 3H_2O$$

This reaction seems to be a tenth order reaction but actually it is a second order reaction. This indicates that the reaction takes place in several steps.

Rate Determining Step

As discussed above, even a simple looking reaction might have been proceeding through several steps. Out of these steps, the slowest step of the reaction is considered as the rate determining step of the chemical reaction and decides the overall rate of the reaction. Consider the following reaction,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

The rate law for this equation is found to be,

$$\text{Rate of reaction} = k[N_2O_5]$$

If the reaction occur by the collisions of two N_2O_5 molecules as indicated by the balanced equation, it would be a second order reaction as Rate $= k[N_2O_5]^2$

But observed rate law suggests that it is a first order reaction which implies that the reaction is a complex reaction. So, it must take place in two steps in such a way that the slowest step should involve only one molecule of N_2O_5.

Step I $N_2O_5 \xrightarrow{\text{Slow}} NO_2 + NO_3$

Step II $N_2O_5 + NO_3 \xrightarrow{\text{Fast}} 3NO_2 + O_2$

The first step, being slow, is the rate determining step. Since, the rate determining step is unimolecular, so it has order one. The rate of reaction depends not only on the reactants but may also depend upon the substances present as a catalyst.

e.g. Decomposition of H_2O_2, which is catalysed by I^- ion in an alkaline medium.

$$2H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2H_2O + O_2$$

The rate equation for this reaction is found to be,

$$\text{Rate} = \frac{-d[H_2O_2]}{dt} = k[H_2O_2][I^-]$$

This reaction is first order with respect to both H_2O_2 and I^-. Evidences suggest that this reaction takes place in two steps:

Step I $H_2O_2 + I^- \xrightarrow{\text{Slow}} H_2O + IO^-$

Step II $H_2O_2 + IO^- \xrightarrow{\text{Fast}} H_2O + I^- + O_2$

The first step is slow, so it is rate determining step. Species IO^- is called as an intermediate, since it is formed during the course of the reaction but not in the overall balanced equation. Hence, rate of formation of the intermediate will determine the rate of this reaction. It is concluded that, order of complex reactions is determined from the slowest step. Molecularity of the slowest step is equal to the order of the overall reaction.

From these observations, we can distinguish between molecularity and order of a reaction as follows:

S.No.	Molecularity	Order
1.	The number of reacting species which must collide simultaneously in order to carry out a chemical reaction is called molecularity of a reaction.	The sum of powers of the concentrations of the reactants in the rate law expression is called the order of that chemical reaction.
2.	Molecularity is always a whole number value only i.e. 1, 2, 3	Order of reaction may have zero, whole number or fractional values.
3.	Molecularity is a theoretical concept.	Order of reaction is determined experimentally.
4.	Molecularity is applicable to elementary reactions. For complex reactions, it has no meaning.	Order of reaction is applicable to elementary as well as complex reactions.
5.	For simple reactions, molecularity can be obtained from the stoichiometry of the equations.	For simple reactions, order of reaction may not be equal to the number of molecules of the reactants as seen from the balanced equation.
6.	Molecularity of a reaction cannot be zero.	Order of a reaction can be zero.

TOPIC PRACTICE 2

OBJECTIVE Type Questions

1. Find the order of the reaction whose rate constant is $2.5 \times 10^{-2}\ \text{min}^{-1}$.
(a) zero
(b) three
(c) two
(d) one

2. For which of the following, the units of rate constant and rate of the reaction are same?
(a) Zero order reaction
(b) First order reaction
(c) Second order reaction
(d) Third order reaction

3. Consider the data given below for a hypothetical reactions, $M \rightarrow N$

Time(s)	Rate of reaction (mol L^{-1} s^{-1})
0	4.20×10^{-4}
10	4.20×10^{-4}
20	4.20×10^{-4}
30	4.20×10^{-4}
40	4.18×10^{-4}

For the above data, the order of reaction is
(a) one
(b) two
(c) three
(d) zero

4. For the elementary reaction $M \rightarrow N$, the rate or disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is
(a) 4 (b) 3 (c) 2 (d) 1

5. For the non-stoichiometric reaction $2A + B \longrightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial concentration of [A]	Initial concentration of [B]	Initial rate of formation of C (mol L^{-1} s^{-1})
0.1 M	0.1 M	1.2×10^{-3}
0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is
(a) $\frac{dC}{dt} = k[A][B]$ (b) $\frac{dC}{dt} = k[A]^2[B]$
(c) $\frac{dC}{dt} = k[A][B]^2$ (d) $\frac{dC}{dt} = k[A]$

6. The unit of the rate constant of nth order is
(a) $mol^{1-n}\, L^{n-1}\, s^{-1}$ (b) $mol^{n-1}\, L^{1-n}\, s^{-1}$
(c) $mol^{n-1}\, L^{n-1}\, s$ (d) $mol^{n}\, L^{1-n}\, s^{-1}$

7. For the given rate expression $= k[A]^{3/2}[B]^{-1}$, the overall order of a reaction is
(a) zero (b) half (c) one (d) two

8. The reaction,
$$2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2 \text{ is}$$
(a) bimolecular and first order
(b) unimolecular and second order
(c) bimolecular and second order
(d) unimolecular and first order

VERY SHORT ANSWER Type Questions

9. For a certain reaction, the rate law is, Rate $= k[A][B]^{3/2}$. Can this belongs to an elementary reaction? **NCERT Exemplar**

10. Write the rate equation for the reaction, $2A + B \longrightarrow C$, if the order of the reaction is zero. **NCERT Exemplar**

11. Molecularity of any reaction not be equal to zero? **NCERT Exemplar**

12. For which type of reactions, order and molecularity have the same value? **NCERT Exemplar**

13. In a reaction, if the concentration of the reactant R is quadrupled, the rate of reaction becomes sixty four times. What is the order of reaction?

14. Define order of reaction. Write the condition under which a bimolecular reaction follows first order kinetics. **Delhi 2020**

15. For a reaction, $A + B \longrightarrow$ product, the rate law is given by, $r = k[A]^{1/2}[B]^2$. What is the order of the reaction? **NCERT Intext; All India 2013**

SHORT ANSWER Type I Questions

16. We do not determine the order of a reaction by taking into consideration the balanced chemical equation? Give reason. **NCERT Exemplar**

17. For a reaction : $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$
Rate $= k$
(i) Write the order and molecularity of this reaction.
(ii) Write the unit of k. **All India 2016C**

18. A reaction is of second order with respect to a reactant. How is the rate of reaction affected, if the concentration of the reactant is
(i) doubled ?
(ii) reduced to half ? **NCERT**

19. The conversion of molecules x to y follows second order kinetics. If concentration of x is increased to three times, how will it affect the rate of formation of y ? **NCERT Intext**

20. (i) Distinguish between order and molecularity.
(ii) Why is the probability of reaction with molecularity higher than three, is very rare? **Delhi 2020**

SHORT ANSWER Type II Questions

21. The reaction between A and B is of first order with respect to A and zero order with respect to B. Fill in the blanks in the following table.

Exp. No.	[A] /mol L^{-1}	[B] /mol L^{-1}	Initial rate/ mol L^{-1} min^{-1}
1.	0.1	0.1	2.0×10^{-2}
2.	—	0.2	4.0×10^{-2}
3.	0.4	0.4	—
4.	—	0.2	2.0×10^{-2}

NCERT

22. In a reaction between A and B, the initial rate of reaction (r_0) was measured for different initial concentrations of A and B as given below:

A/mol L^{-1}	0.20	0.20	0.40
B/mol L^{-1}	0.30	0.10	0.05
r_0/mol L^{-1} s^{-1}	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of the reaction with respect to A and B? **NCERT**

23. A reaction is of second order in A and first order in B.
(i) Write the differential rate equation.
(ii) How is the rate affected on increasing the concentration of A three times?
(iii) How is the rate affected when the concentration of both A and B is doubled? **Delhi 2013**

LONG ANSWER Type Question

24. Consider the following reaction,

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

The rate of reaction becomes doubled when the concentration of Cl_2 is doubled. However, when the concentration of both the reactants are doubled, the rate becomes eight times. What is the order with respect to NO and with respect to reactant chlorine? What is the overall order of reaction?

HINTS AND EXPLANATIONS

1. (*d*) The value of $k = 2.5 \times 10^{-2}$ min^{-1} carries the unit of time alone and therefore it is a first order reaction.

2. (*a*) The units of rate constant and rate of a reaction are same for zero order reaction.

3. (*d*) As the rate of the reaction remains constant with time, therefore, reaction is of zero order.

4. (*b*) For elementary reaction, $M \rightarrow N$

Rate law can be written as rate $\propto [M]^n$

$$\text{Rate} = k[M]^n \quad \text{...(i)}$$

When we double the concentration of $[M]$, rate becomes 8 times, hence, new rate law can be written as

$$8 \times \text{rate} = k\,[2M]^n$$

$$\therefore \quad \frac{1}{8} = \frac{1}{[2]^n} \Rightarrow 2^n = 8 = 2^3 \Rightarrow n = 3$$

5. (*d*) This problem can be solved by determining the order of reaction with respect to each reactant and then writing rate law equation of the given equation accordingly as,

$$R = \frac{dC}{dt} = k[A]^x[B]^y$$

where, x = order of reaction w.r.t $A = 1$
y = order of reaction w.r.t $B = 0$

6. (*a*) The units of rate constant of nth order is mol^{1-n} $L^{n-1}s^{-1}$.

7. (*b*) Rate $= k[A]^x\,[B]^y$
order $= x + y$

$\therefore$ Order is $\left(\frac{3}{2}\right) + (-1) = 1/2$, i.e. half-order.

8. (*a*) $2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2$ is a bimolecular and first order reaction.

9. For an elementary reaction, order of reaction must be equal to the molecularity but molecularity should be integral. For the given rate law, order of reaction comes out to be 5/2 [1 + 3/2]. As molecularity cannot be fractional. Therefore, order is not equal to molecularity. Hence, the given rate law does not belong to an elementary reaction.

10. The rate equation for the given reaction is rate $= k[A]^0[B]^0 = k$

11. Molecularity of the reaction is the number of molecules taking part in an elementary step. For this we require at least a single molecule leading to the value of minimum molecularity of one. Hence, molecularity of any reaction can never be equal to zero.

12. For elementary reaction, i.e. the reaction which proceeds in a single step, order and molecularity have the same value.

13. $r_1 = k(R)^r$, $r_2 = k(4R)^r$

On dividing r_2 by r_1, we get

$$\frac{r_2}{r_1} = \frac{k(4R)^r}{k(R)^r} = 64 = (4)^r$$

$$\Rightarrow \quad (4)^3 = (4)^r \Rightarrow r = 3$$

14. Refer to page 101 (Order of reaction).
A bimolecular reaction can be kinetically first order in behaviour provided one of the reactant is taken in such a large excess that its concentration may hardly change. Such a reactant will not contribute to the order of reaction.

15. Order of reaction $= \frac{1}{2} + 2 = \frac{5}{2}$

Hence, order $= \frac{5}{2}$

16. The rate of reaction may not depend upon all the molecules of a reactant present in the balanced chemical equation. Thus, balanced chemical equation often leads to incorrect order or rate law.

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

This is actually a fourth order reaction but it seems to be a twelfth order reaction. Actually, the reaction is complex and occurs in several steps. The order of such reaction is determined by the slowest step in the reaction mechanism.

17. (i) For a reaction, $H_2 + Cl_2 \xrightarrow{hv} 2HCl$

Rate $= k$, suggests that the reaction is of zero order. Further, the molecularity of a given reaction is 2 as two molecules are participating in the reaction. Hence, order = zero and molecularity = two.

(ii) The unit of k for zero order reaction is equal to the rate of a reaction which is mol $L^{-1}s^{-1}$. Hence, the unit of k for the given reaction is mol $L^{-1}s^{-1}$.

18. (i) If the concentration of reactant A is doubled,

i.e. $[A] = 2a$

Then, rate $= k(2a)^2 = 4\,ka^2$

Rate of reaction becomes 4 times.

(ii) When concentration of A is reduced to $\frac{1}{2}$,

i.e. $[A] = \frac{1}{2}a$

$\Rightarrow$ rate $= k\left(\frac{a}{2}\right)^2 = \frac{1}{4}ka^2$

Rate of reaction becomes $\frac{1}{4}$ times, i.e. reduced to one-fourth.

19. For the reaction, $x \rightarrow y$

Reaction rate, $(r) = k[x]^2$ (for II order) ...(i)

If the concentration of x is increased three times, then

Reaction rate, $(r') = k[3x]^2 = k \times [9x^2]$ ...(ii)

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{r'}{r} = \frac{k \times [9x^2]}{k \times [x^2]} = 9$$

It means that the rate of formation of y will increase by nine times.

20. (i) Refer to text on pages 103.

(ii) Refer to text on page 102.

21. The rate expression, Rate $= k[A]^1[B]^0 = k[A]$

For experiment 1, $[A] = 0.1$ mol L^{-1}

So, rate $= 2.0 \times 10^{-2} = k\,[0.1 \text{ mol } L^{-1}]$

$\therefore \quad k = \frac{2.0 \times 10^{-2} \text{ mol } L^{-1}\text{min}^{-1}}{0.1 \text{ mol } L^{-1}} = 0.2 \text{ min}^{-1}$

For experiment 2, rate $= k[A]$

4.0×10^{-2} mol L^{-1}min^{-1} $= 0.2$ min$^{-1}[A]$

$$[A] = \frac{4.0 \times 10^{-2} \text{ mol } L^{-1}\text{min}^{-1}}{0.2 \text{ min}^{-1}} = 0.2 \text{ mol } L^{-1}$$

$[A] = 0.2$ mol L^{-1}

For experiment 3, rate $= k[A]$

Rate $= 0.2$ min$^{-1} \times 0.4$ mol L^{-1}

Rate $= 8 \times 10^{-2}$ mol L^{-1}min^{-1}

For experiment 4, rate $= k[A]$

$\Rightarrow [A] = \frac{\text{Rate}}{k} \Rightarrow [A] = \frac{2.0 \times 10^{-2}}{0.2} = 0.1$ mol L^{-1}

22. Rate law states that rate $= k[A]^x[B]^y$

$(\text{Rate})_1 = k[0.20]^x[0.30]^y = 5.07 \times 10^{-5}$ ...(i)

$(\text{Rate})_2 = k[0.20]^x[0.10]^y = 5.07 \times 10^{-5}$ ...(ii)

$(\text{Rate})_3 = k[0.40]^x[0.05]^y = 1.43 \times 10^{-4}$ ...(iii)

On dividing Eq. (i) by Eq. (ii), we get

$$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{k[0.20]^x[0.30]^y}{k[0.20]^x[0.10]^y} = \frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = 1$$

$$[3]^y = [3]^0$$

$$y = 0$$

Now, on dividing Eq. (iii) by Eq. (ii), we get

$$\frac{(\text{Rate})_3}{(\text{Rate})_2} = \frac{k(0.40)^x(0.05)^0}{k(0.20)^x(0.10)^0} = \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}}$$

$$2.8205 = 2^x\left(\frac{1}{2}\right)^0 = 2^x$$

$$\log 2.8205 = x \log 2$$

$$x = \frac{0.4503}{0.3010} = 1.5$$

Thus, order of the reaction with respect to A and B are 1.5 and 0, respectively.

23. A reaction is second order in A and first order in B.

(i) Differential rate equation,

$$\text{Rate} = -\frac{d[R]}{dt} = k[A]^2[B]$$

(ii) When the concentration of A is increased three times, i.e. $3A$, then

Rate $= k[3A]^2[B] = 9k[A]^2[B] = 9(\text{rate})$

This shows that rate will increase 9 times to the initial rate.

(iii) When concentration of both A and B is doubled then,

Rate $= k[2A]^2[2B] = 8k[A]^2[B] = 8(\text{rate})$

This shows that rate will increase 8 times to the initial rate.

24. $2NO(g)+Cl_2(g) \longrightarrow 2NOCl(g)$

Let the rate of reaction be

$$r_1 = k[NO]^{\alpha}[Cl_2]^{\beta} \quad \text{...(i)}$$

$$r_2 = 2r_1 = k[NO]^{\alpha}[2Cl_2]^{\beta} \quad \text{...(ii)}$$

$$r_3 = 8r_1 = k[2NO]^{\alpha}[2Cl_2]^{\beta} \quad \text{...(iii)}$$

On dividing Eq. (ii) by Eq. (i), we get

$$\frac{r_2}{r_1} = \frac{2r_1}{r_1} = \frac{k[NO]^{\alpha}\cdot[2Cl_2]^{\beta}}{k[NO]^{\alpha}\cdot[Cl_2]^{\beta}}$$

$$\therefore \quad (2)^1 = (2)^{\beta} \Rightarrow \beta = 1$$

Similarly, on dividing Eq. (iii) by Eq. (i), we get

$$\frac{r_3}{r_1} = \frac{8r_1}{r_1} = \frac{k[2NO]^{\alpha}\cdot[2Cl_2]^{\beta}}{k[NO]^{\alpha}\cdot[Cl_2]^{\beta}}$$

$$8 = (2)^{\alpha}\cdot(2)^{\beta}$$

$$8 = (2)^{\alpha}\cdot(2)^1;\ 4 = (2)^{\alpha}$$

$$(2)^2 = (2)^{\alpha};\ \alpha = 2$$

$$\therefore \quad r = k[NO]^2[Cl_2]^1$$

As, order with respect to $NO = 2$

Order with respect to $Cl_2 = 1$

Overall order of reaction $= 2+1 = 3$.

|TOPIC 3|
Integrated Rate Equation

The concentration dependence of rate is called **differential rate equation**. It is not always convenient to determine the instantaneous rate as it is measured by determination of slope of the tangent at point t in concentration *vs* time plot. Thus, it becomes difficult to determine the rate law and hence the order of the reaction.

Thus, the differential rate equation is integrated to get a relation between directly measured experimental data, i.e. concentrations at different time and rate constant. The integrated rate equations are different for the reactions of different reaction orders.

The integrated equation is used for determining the rate constant of the reaction. In this topic, we shall determine these equations only for zero and first order chemical reactions. The resultant equation is called integrated rated equation.

ZERO ORDER REACTIONS

It means that the rate of the reaction is proportional to zero power of the concentration of reactants.

Thus, in zero order reaction, the rate does not depend on the concentration of any of the reactants.

Consider the reaction,

$$R \longrightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0 = k \times 1$$

$$d[R] = -k\,dt$$

On integrating both sides,

$$[R] = -kt + I \quad \text{...(i)}$$

where, I is the constant of integration.

Initially, at $t=0$, the concentration of the reactant $R=[R]_0$, where R_0 is the initial concentration of the reactant.

From Eq. (i), we have

$$[R]_0 = -k \times 0 + I$$

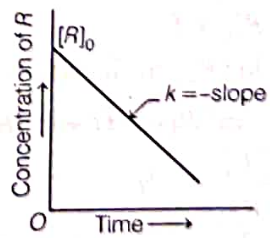
On substituting, $[R]_0 = I$ in the Eq.(i) we get

$$[R] = -kt + [R]_0 \quad \text{...(ii)}$$

Simplifying Eq. (ii), gives

$$k = \frac{[R]_0 - [R]}{t} \quad \text{...(iii)}$$

If we plot $[R]$ against t, we get a straight line with slope equal to $-k$ and intercept equal to $[R]_0$ as shown in the below figure.



Variation in the concentration *vs* time plot for a zero order reaction

(i) Zero order reactions are not so common and they occur under special conditions.

Some enzyme catalysed reactions and reactions which occur on metal surfaces are few examples of zero order reactions, e.g. decomposition of gaseous ammonia on platinum surface at high temperature and pressure.

$$2NH_3(g) \xrightarrow{1130\,K,\,Pt\ catalyst} N_2(g) + 3H_2(g)$$

$$\text{Rate} = k[NH_3]^0 = k$$

Note The decomposition of NH_3 on finely divided platinum surface is of first order when concentration (pressure) of NH_3 is low.

In this reaction, at high pressure, surface of platinum catalyst is saturated with ammonia (gas) molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration.

(ii) The thermal decomposition of HI on gold surface is another example of zero order reaction.

$$2HI \xrightarrow{Gold} H_2 + I_2$$

(iii) Reaction between hydrogen and chlorine under the influence of UV-light

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl$$

FIRST ORDER REACTIONS

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant, R. For the reaction, $R \longrightarrow P$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R] \text{ or } \frac{d[R]}{[R]} = -kdt$$

On integrating the equation, we get

$$\ln[R] = -kt + I \quad \ldots\text{(i)}$$

where, I is the constant of integration.

In the beginning when $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant.

$\therefore$ Eq. (i) can be rewritten as

$$\ln[R]_0 = -k \times 0 + I$$

$$\ln[R]_0 = I$$

On substituting $I = \ln[R]_0$ in the Eq. (i) to get

$$\ln[R] = -kt + \ln[R]_0 \quad \ldots\text{(ii)}$$

or $$\ln\frac{[R]}{[R]_0} = -kt \quad \ldots\text{(iii)}$$

or $$\frac{1}{t}\ln\frac{[R]}{[R]_0} = -k \text{ or } k = \frac{1}{t}\ln\frac{[R]_0}{[R]} \quad \ldots\text{(iv)}$$

or $$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} \quad \ldots\text{(v)}$$

This Eq. (v) is usually written as:

$$k = \frac{2.303}{t}\log\frac{[N]_0}{[N]} \quad \text{or} \quad k = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

where, a is the initial concentration of reactant, R and $(a-x)$ is the concentration of reactant R, left after time t as x moles of it get changed to products after time t.

i.e. $[R]_0 = [N]_0 = a$ and $[R] = [N] = (a-x)$

Expression for Rate Constant at Time t_1 and t_2

Rate constant can be calculated if concentrations of the reactants are measured at time t_1 and t_2.

At time t_1, $\ln[R]_1 = -kt_1 + \ln[R]_0 \quad \ldots\text{(vi)}$

At time t_2, $\ln[R]_2 = -kt_2 + \ln[R]_0 \quad \ldots\text{(vii)}$

Here, $[R]_1$ and $[R]_2$ are concentrations of the reactants at time t_1 and t_2, respectively.

On subtracting Eq. (vi) from Eq. (vii), we have

$$\ln[R]_1 - \ln[R]_2 = -kt_1 - (-kt_2)$$

or, $$\ln\frac{[R]_1}{[R]_2} = k(t_2 - t_1)$$

$$k = \frac{1}{t_2 - t_1}\ln\frac{[R]_1}{[R]_2} \quad \ldots\text{(viii)}$$

$$k = \frac{2.303}{t_2 - t_1}\log\frac{[R]_1}{[R]_2}$$

Exponential form of Eq. (iii) can be written as:

$$[R] = [R]_0 e^{-kt} \quad \ldots\text{(ix)}$$

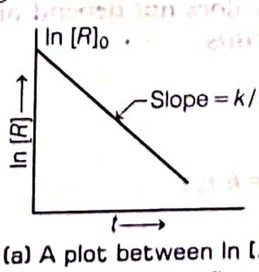
If we plot $\ln[R]$ against t, we get a straight line with slope $= -k$ and intercept equal to $\ln[R]_0$ as shown in figure (a).

The first order rate Eq. (iv) can also be written as:

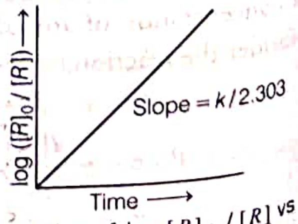
$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} \quad \ldots\text{(x)}$$

or $$\log\frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

If we plot a graph between $\log[R]_0/[R]$ *vs* t, we get a straight line with the slope $= k/2.303$ as shown in figure (b).



(a) A plot between ln $[R]$ and time (t) for a first order reaction



(b) Plot of $\log[R]_0/[R]$ vs time for a first order reaction

Examples of the First Order Reactions

(i) All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

$$^{226}_{88}Ra \longrightarrow \, ^{4}_{2}He + \, ^{222}_{86}Rn$$

$$\text{Rate} = k\,[Ra]$$

(ii) Hydrogenation of ethene and decomposition of N_2O_5 and N_2O are more examples of first order reactions.

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g); \quad \text{Rate} = k[C_2H_4]$$

$$N_2O_5(g) \longrightarrow N_2O_5(g) + \frac{1}{2}O_2(g); \text{Rate} = k[N_2O_5]$$

$$N_2O(g) \longrightarrow N_2(g) + \frac{1}{2}O_2(g); \quad \text{Rate} = k[N_2O]$$

EXAMPLE |1| Consider a certain reaction $A \longrightarrow$ products, with $k = 2.0 \times 10^{-2} s^{-1}$. Calculate the concentration of A remaining after 100 s if the initial concentration of A is $1.0 \text{ mol } L^{-1}$. **NCERT**

Sol. $k = 2.0 \times 10^{-2} s^{-1}$; $[A]_0 = 1.0 \text{ mol } L^{-1}$; $t = 100$ s

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

Therefore,

$$2.0 \times 10^{-2} s^{-1} = \frac{2.303}{100 \text{ s}} \log \frac{1.0 \text{ mol } L^{-1}}{[A]}$$

$$2.0 \times 10^{-2} s^{-1} = \frac{2.303}{100 \text{ s}} (\log 1 - \log [A])$$

$$2.0 \times 10^{-2} s^{-1} = \frac{2.303}{100 \text{ s}} (0 - \log [A])$$

$$-\log [A] = \frac{2.0 \times 10^{-2} s^{-1} \times 100 \text{ s}}{2.303}$$

or $$[A] = \text{antilog}\left(-\frac{2.0 \times 10^{-2} s^{-1} \times 100 \text{ s}}{2.303}\right)$$

or $$[A] = 0.135 \text{ mol } L^{-1}$$

Pressure Change Method for the Calculation of the Value of Rate Constant

Let us consider a typical first order gas phase reaction,

$$A(g) \longrightarrow B(g) + C(g)$$

Let p_i be the initial pressure of A at time $t = 0$ and p_t be the total pressure at time, t. Integrated rate equation for such a reaction can be derived as :

Total pressure, $p_t = p_A + p_B + p_C$ (pressure units)

where p_A, p_B and p_C are the partial pressures of A, B and C, respectively.

If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, then increase in pressure of B and C will also be x atm each.

	$A(g)$	$\longrightarrow$	$B(g)$	+	$C(g)$
At $t = 0$	p_i atm		0 atm		0 atm
At time t	$(p_i - x)$ atm		x atm		x atm

$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

where, $p_A = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$

$$k = \left(\frac{2.303}{t}\right)\left(\log \frac{p_i}{p_A}\right)$$

$$\boxed{k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}}$$

EXAMPLE |2| The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume,

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Exp. No.	Time/s^{-1}	Total pressure/atm
1.	0	0.5
2.	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm. **NCERT**

Sol.

	$SO_2Cl_2(g)$	$\longrightarrow$	$SO_2(g)$	+	$Cl_2(g)$
Initially at $t = 0$	p_i		0		0
After time t	$p_i - p$		p		p

Total pressure after time t, i.e.

$$p_t = p_i - p + p + p = p_i + p$$

$$\therefore \quad p = p_t - p_i$$

So, $$p_{SO_2Cl_2} = p_i - p$$
$$= p_i - (p_t - p_i)$$
$$= p_i - p_t + p_i$$
$$= 2p_i - p_t$$

Substitutions of the value of a and $(a - x)$ gives

$$k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

(a) Calculation of rate constant, k

Given, $p_i = 0.5$ atm; $p_t = 0.6$ atm

$$k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

$$= \frac{2.303}{(100 \text{ s})} \log \frac{0.5 \text{ atm}}{0.4 \text{ atm}} = \frac{2.303}{(100 \text{ s})} \log 1.25$$

$$= \frac{2.303}{(100 \text{ s})} \times 0.0969 = 2.23 \times 10^{-3} s^{-1}$$

(b) Calculation of reaction rate when total pressure is 0.65 atm

$$p_{SO_2Cl_2} = 0.5-(0.65-0.50)$$
$$= (1-0.65) = 0.35 \text{ atm}$$
$$k = 2.23\times10^{-3}\text{s}^{-1}$$
$$\text{Rate} = k\times p_{SO_2Cl_2} = (2.23\times10^{-3}\text{s}^{-1})\times(0.35\text{ atm})$$
$$\text{Rate} = 7.8\times10^{-4}\text{ atm s}^{-1}$$

HALF-LIFE OF A REACTION

The time in which the concentration of a reactant is reduced to one-half of its initial concentration is called the half-life of a reaction. It is represented as $t_{1/2}$.

For a zero order reaction,

$$k = \frac{[R]_0 - [R]}{t}$$

At $t = t_{1/2}$, $\quad [R] = \frac{1}{2}[R]_0$

The rate constant at $t_{1/2}$ becomes

$$k = \frac{[R]_0 - 1/2[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

For the first order reaction,

$$k = \frac{1}{t}\ln\frac{[R]_0}{[R]}$$

or $$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

At $t_{1/2}$, $\quad [R] = \frac{R_0}{2}$

Therefore, $$k = \frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]_0/2}$$

or $$k = \frac{2.303}{t_{1/2}}\log 2$$

or $$k = \frac{2.303}{t_{1/2}}\times 0.301$$

or $$\boxed{t_{1/2} = \frac{0.693}{k}}$$

Thus, for first order reaction, $t_{1/2}$ is independent of $[R]_0$ and hence, constant.

The half-life of a reaction with nth order is given as:

$$t_{1/2} \propto \frac{1}{[R]_0^{n-1}}$$

Therefore, for zero order reaction $t_{1/2} \propto [R]_0$. For first order reaction, $t_{1/2}$ is independent of $[R_0]$. For second order reaction $t_{1/2} \propto \frac{1}{[R_0]}$ and so on.

EXAMPLE |3| The half-life for radioactive decay of ^{14}C is 5730 yr. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Calculate the age of the sample. **NCERT**

> (i) Since, all the radioactive processes follow first order kinetics, rate constant from $t_{1/2}$ can be calculated as :
> $k = 0.693/t_{1/2}$
> (ii) Then, put the value of k in the expression of first order rate constant to find t.

Sol. $$t_{1/2} = \frac{0.693}{k} \quad \text{(For first order reaction)}$$

$$\therefore \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}\text{yr}^{-1}$$

We know that,

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} = \frac{2.303}{\frac{0.693}{5730}}\log\frac{100}{80} \quad \left(\text{As, } k = \frac{0.693}{t_{1/2}}\right)$$

$$= \frac{2.303\times5730}{0.693}\log\frac{100}{80} = \frac{2.303\times5730}{0.693}\log 1.25$$

$$= \frac{2.303\times5730}{0.693}\times0.0969$$

$$= 1845 \text{ yr (approx.)}$$

Therefore, the age of the given archaeological artifact containing wood is 1845 yr.

Integrated rate laws for the reactions of zero and first order

Order	0	1
Reaction type	$R \rightarrow P$	$R \rightarrow P$
Differential rate law	$d[R]/dt = -k$	$d[R]/dt = -k[R]$
Integrated rate law	$kt = [R]_0 - [R]$	$[R] = [R]_0 e^{-kt}$ or or $kt = \ln\{[R]_0/[R]\}$
Straight line plot	$[R]$ vs t	$\ln [R]$ vs t
Half-life	$[R]_0/2k$	$\ln 2/k$
Units of k	conc. time^{-1} or mol L^{-1}s^{-1}	time^{-1} or s^{-1}

PSEUDO FIRST ORDER REACTION

The reactions which are not actually of first order but behave so due to altered conditions are called pseudo first order reactions. In such a chemical reaction between two substances, one reactant is present in large or excess amounts.

e.g. When 0.01 mole of ethyl acetate is hydrolysed with 10 moles of water, amounts of the various constituents at the beginning ($t = 0$) and completion (t) of the reaction are mentioned below:

	$CH_3COOC_2H_5$	$+ H_2O \xrightarrow{H^+}$	CH_3COOH	$+ C_2H_5OH$
$t = 0$	0.01mol	10 mol	0 mol	0 mol
t	0 mol	9.99 mol	0.01mol	0.01mol

The concentration of water is not considered in calculation as its concentration does not get altered much during the course of reaction.

$$\text{Rate} = k' [CH_3COOC_2H_5][H_2O] \quad ...(i)$$

But term $[H_2O]$ can be taken as constant, then Eq. (i) becomes $\text{Rate} = k[CH_3COOC_2H_5]$, where $k = k'[H_2O]$

The reaction behaves as first order reaction. Such reactions are pseudo first order reactions. Inversion of cane sugar is another pseudo first order reaction.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\text{Rate} = k[C_{12}H_{22}O_{11}]$$

EXAMPLE |4| In a pseudo first order hydrolysis of an ester in water, the following results were obtained :

t/s	0	30	60	90
[Ester]/mol L^{-1}	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 s.

(ii) Calculate the pseudo first order rate constant for the hydrolysis of an ester. **NCERT**

Sol. (i) Average rate during the interval 30-60 s.

$$\frac{C_2 - C_1}{t_2 - t_1} = \frac{0.31 - 0.17}{60 - 30}$$

$$= \frac{0.14}{30} \text{ mol L}^{-1}\text{s}^{-1}$$

$$= 4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

(ii) $k' = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$

Here, $[A]_0 = 0.55, t = 30$

$$k = \frac{2.303}{30} \log \frac{0.55}{0.31} = 1.91 \times 10^{-2} \text{s}^{-1}$$

$$t = 60 \text{ s}, \quad k' = \frac{2.303}{60} \log \frac{0.55}{0.17} = 1.96 \times 10^{-2} \text{s}^{-1}$$

$$t = 90 \text{ s}, \quad k' = \frac{2.303}{60} \log \frac{0.55}{0.085} = 2.07 \times 10^{-2} \text{s}^{-1}$$

$$\text{Average } k' = \frac{1.91 + 1.96 + 2.07}{3} \times 10^{-2}$$

$$= 1.98 \times 10^{-2} \text{s}^{-1}$$

TOPIC PRACTICE 3

OBJECTIVE Type Questions

1. The slope of the plot of ln $[R]$ *vs* time gives **All India 2020**

(a) $+k$ (b) $\frac{+k}{2.303}$ (c) $-k$ (d) $\frac{-k}{2.303}$

2. Four reactions are given below. Which one of them is of zero order?

(a) $PCl_5 \longrightarrow PCl_3 + Cl_2$

(b) $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

(c) $H_2 + Cl_2 \longrightarrow 2HCl$

(d) $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2} O_2$

3. The rate constant of the reaction, $A \rightarrow B$ is 0.6×10^{-3} mole per second. If the concentration of A is 5 M then concentration of B after 20 min is

(a) 1.08 M (b) 3.60 M

(c) 0.36 M (d) 0.72 M

4. Equation for rate constant of a first order reaction is

Or The equation of velocity constant (k) for first order reaction is

(a) $k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$ (b) $k = \frac{4.306}{t} \log_{10} \frac{a}{(a-x)}$

(c) $k = \frac{2.303}{t^2} \log_{10} \frac{a}{(a-x)}$ (d) $k = \frac{10}{t} \log_{10} \frac{a}{(a-x)}$

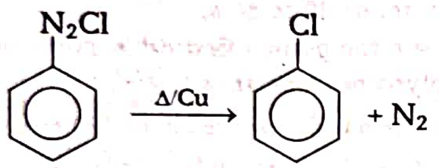
5. Consider a first order gas phase decomposition reaction given below **NCERT Exemplar**

$$A(g) \rightarrow B(g) + C(g)$$

The initial pressure of the system before decomposition of A was p_i. After lapse of time 't' total pressure of the system increased by x units and became 'p_t'. The rate constant k for the reaction is given as ....

(a) $k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$ (b) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$
(c) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i + p_t}$ (d) $k = \frac{2.303}{t} \log \frac{p_i}{p_i + x}$

6. For the reaction,



half-life does not depend on the concentration of the reactant. After 10 min, volume of N_2 gas is 20 L and after the completion of reaction, it is 100 L. Hence, rate constant is
(a) $\frac{2.303}{10} \log 5 \text{ min}^{-1}$ (b) $\frac{2.303}{10} \log 10 \text{ min}^{-1}$
(c) $\frac{2.303}{10} \log 10 \text{ min}^{-1}$ (d) $\frac{2.303}{10} \log 20 \text{ min}^{-1}$

7. Time taken to complete 90% of first order reaction is

Or The time taken for the 90% completion of a first order reaction is approximately
(a) 2.2 of half-life period (b) 3.3 of half-life period
(c) 1.1 of half-life period (d) 4.4 of half-life period

8. Expression for the half-life of zero order reaction is given as
(a) $t_{1/2} = \frac{[R]}{2k}$ (b) $t_{1/2} = \frac{[R]_0}{2k}$
(c) $t_{1/2} = \frac{0.693}{k}$ (d) $t_{1/2} = \frac{0.301}{k}$

9. When one reactant is present in large excess in a chemical reaction between two substances, then the reaction is known as
(a) first order reaction
(b) second order reaction
(c) zero order reaction
(d) pseudo first order reaction

VERY SHORT ANSWER Type Questions

10. A plot of rate of reaction (Y-axis) *versus* concentration of reactant (X-axis) gives a line parallel to X-axis. What is the order of reaction?

11. A chemical reaction occurs between reactants A and B but the rate does not depend on the concentration of any of the reactants. Can you predict the order of the reaction?

12. A first order reaction takes 30 minutes for 20% decomposition. Calculate $t_{1/2}$. [$\log 2 = 0.3010$] **All India 2019**

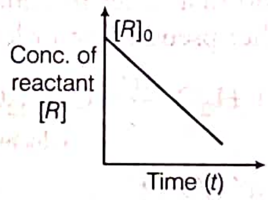
13. What is the order of a reaction that is 50% complete after 2 h and 75% complete after 4 h?

14. For a reaction $R \rightarrow P$, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction? **Delhi 2017**

15. Time required to decompose SO_2Cl_2 to half of its initial amount is 60 min. If the decomposition is a first order reaction, calculate the rate constant of the reaction. **NCERT Intext**

SHORT ANSWER Type I Questions

16. A reaction, reactant $\longrightarrow$ product is represented by (the graph)
All India 2019, NCERT Exemplar; Delhi 2014
(i) Predict the order of the reaction in this case.
(ii) What does the slope of the graph represent? Write the unit of the represented quantity.



All India 2019

17. The decomposition of NH_3 on platinum surface,
$2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$ is a zero order with $k = 2.5 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$. What are the rates of production of N_2 and H_2? **NCERT**

18. Derive integrated rate equation for rate constant of a first order reaction. **All India 2017C**

19. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$. **NCERT; Delhi 2013**

20. The C-14 content of an ancient piece of wood was found to have three tenths of that in living trees. How old is that piece of wood ? ($\log 3 = 0.4771$, $\log 7 = 0.8540$, half-life of C-14 = 5730 years) **CBSE SQP 2021**

21. Calculate the half-life of a first order reaction from their rate constants given below:
(i) 200 s^{-1} (ii) 2 min^{-1} (iii) 4 yr^{-1} **NCERT**

SHORT ANSWER Type II Questions

22. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed.
Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$ **All India 2017**

23. For the first order thermal decomposition reaction, the following data obtained:
$$C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$$

Time/s	Total pressure/atm
0	0.30
300	0.50

Calculate the rate constant. (Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$) **All India 2016**

24. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:
$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.
(Given, $\log 4 = 0.6021$, $\log 2 = 0.3010$)
Delhi 2017, 14, All India 2014, Foreign 2014

25. For a first order reaction, show that the time required for 99% completion is twice the time required for the completion of 90% of reaction.
NCERT; All India 2017C, Delhi 2013

26. A first order reaction has a rate constant $1.15 \times 10^{-3}\ s^{-1}$. How long will 5 g of this reactant take to reduce to 3 g? **NCERT Intext**

27. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2} = 3$ h. What fraction of sample of sucrose remains after 8h? **NCERT**

28. Following data are obtained for the reaction:
$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

t/s	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(i) Show that it follows first order reaction.
(ii) Calculate the half-life.
(Given: $\log 2 = 0.3010$, $\log 4 = 0.6021$) **Delhi 2017**

29. A first order reaction is 25% complete in 40 minutes. Calculate the value of rate constant. In what time will the reaction be 80% completed? **Delhi 2020**

LONG ANSWER Type Questions

30. For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data is obtained:

t (s)	p(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant. **NCERT**

31. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 yr. If 1μ g of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 yr and 60 yr if it is not lost metabolically?
NCERT

32. The experimental data for the decomposition of
$$N_2O_5, [2N_2O_5 \longrightarrow 4NO_2 + O_2]$$
in gas phase of 318 K are given below: **NCERT**

t/s	$10^{-2} \times [N_2O_5]$ /mol L^{-1}
0	1.63
400	1.36
800	1.14
1200	0.93
1600	0.78
2000	0.64
2400	0.53
2800	0.43
3200	0.35

(i) Plot $[N_2O_5]$ against t.
(ii) Find the half-life period for the reaction.
(iii) Draw a graph between $\log [N_2O_5]$ and t.
(iv) What is the rate law?
(v) Calculate the rate constant.
(vi) Calculate the half-life period from k and compare it with (ii).

33. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

t/s	0	30	60
$[CH_3COOCH_3]$/ mol L^{-1}	0.60	0.30	0.15

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

(ii) Calculate the average rate of reaction between the time interval 30 to 60 s.

(Given, log 2 = 0.3010, log 4 = 0.6021)

Delhi 2015

HINTS AND EXPLANATIONS

1. (b) Refer to page 108 (Expression for rate constant at time).

2. (c) $H_2 + Cl_2 \longrightarrow 2HCl$

3. (d) For a zero order reaction unit of rate constant is (mol L^{-1} s^{-1}). Hence, we can easily calculate concentration of B after 20 min by the following formula,

$$[B] = kt = 0.6 \times 10^{-3} \times 20 \times 60 = 0.72 \text{ M}$$

4. (a) For first order reaction, rate constant is

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

where, a = initial concentration of reactant
$(a-x)$ = concentration after time t.

5. (b)

$$\begin{array}{lccc} & A(g) \rightarrow & B(g) + & C(g) \\ \text{Initially} & p_i & 0 & 0 \\ \text{At time } t & p_i - x & x & x \end{array}$$

$p_t = p_i - x + x + x = p_i + x$

For first order reaction $x = p_t - p_i$

$$k = \frac{2.303}{t}\log\frac{p_i}{p_i - x} = \frac{2.303}{t}\log\frac{p_i}{2p_i - p_t}$$

6. (a) As the half-life doesn't depend on concentration of reactants, so it is a first order reaction

Here, $\frac{[R]_0}{[R]} = \frac{100}{20} = 5$

$t = 10$ min

$$k = \frac{2.303}{t}\log\frac{[R_0]}{[R]}$$

or $$k = \frac{2.303}{10 \text{ min}}\log 5$$

7. (b) For first order reaction,

$$t_{1/2} = \frac{0.693}{k} \quad \text{...(i)}$$

where, $t_{1/2}$ is half-life period.

Time taken to complete 90% of reaction is

$$t_{90} = \frac{2.303}{k}\log\frac{100}{(100-90)} = \frac{2.303}{k} \quad \text{...(ii)}$$

By dividing Eq. (ii) by (i), we get

$$\frac{t_{90}}{t_{1/2}} = \frac{2.303}{0.693} = 3.3$$

thus, $t_{90} = 3.3\ t_{1/2}$

8. (b) $t_{1/2} = \frac{[R]_0}{2k}$, for a zero order reaction.

9. (d) Pseudo first order reaction.

10. As the rate of reaction is independent of concentration of reactant, thus, reaction is of zero order.

11. [Hint In zero order reaction, rate does not depend upon the concentration of any reactant].

12. Given, reactant decomposes = 20% in 30 minutes (x)

Let initial quantity $(a) = 100$.

Then after 30 miutes $(a-x) = 100 - 20 = 80$.

Time $(t_{30}) = 30$ minutes

Formula used

$$\frac{t_{1/2}}{t_{30}} = \frac{\log\left[\frac{a}{a-x}\right]_1}{\log\left[\frac{a}{a-x}\right]_2} = \frac{\log 2}{\log\left[\frac{a}{a-x}\right]_2}$$

$$\frac{t_{1/2}}{t_{30}} = \frac{0.3010}{\log\frac{100}{80}} = \frac{0.3010}{1.25}$$

$$\frac{t_{1/2}}{t_{30}} = \frac{0.3010}{0.0969} = 3.106 = 3.00$$

$$\frac{t_{1/2}}{30} = 3.00 \qquad (\because t_{30} = 30 \text{ minutes})$$

$\therefore \quad t_{1/2} = 3.00 \times 30 = 90$

Hence, half-life $(t_{1/2}) = 90$ minutes

13. It is a first order reaction because for 75% completion of reaction two half-lives are required (as, $t_{1/2} = 2$ h), which suggests that $t_{1/2}$ is independent of initial concentration.

14. For a reaction $R \rightarrow P$, half-life $(t_{1/2})$ is observed to be independent of the initial concentration of reactants. Thus, it follow first order reaction.

15. Rate constant

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60 \text{ min}} = \frac{0.693}{(60 \times 60)\text{ s}} = 1.925 \times 10^{-4} s^{-1}$$

16. (i) The reaction is of zero order.

(ii) Slope of the graph $= -k = \frac{d[R]}{dt}$

The unit of k, for zero order reaction is mol $L^{-1}s^{-1}$.

17. $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$

For zero order reaction, rate = k

$$\therefore \text{Rate} = -\frac{1}{2}\frac{d[NH_3]}{dt} = +\frac{d[N_2]}{dt}$$

$$= +\frac{1}{3}\frac{d[H_2]}{dt} = 2.5\times10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}$$

$\therefore$ Rate of production of N_2

$$= \frac{d[N_2]}{dt} = 2.5\times10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}$$

Rate of production of H_2

$$= \frac{1}{3}\frac{d[H_2]}{dt} = 2.5\times10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}$$

$$\frac{d[H_2]}{dt} = 7.5\times10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}$$

18. Refer to text on page 108.

19. Let $a = 100$, $a - x = 100 - 30 = 70$, $t = 40$ min

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)} = \frac{2.303}{40\text{ min}}\log\frac{100}{70}$$

$$= \frac{2.303}{40}\log\frac{10}{7} = \frac{2.303}{40}\log 1.428 = \frac{2.303}{40}\times 0.1548$$

$$k = 8.91\times10^{-3}\text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.91\times10^{-3}\text{min}^{-1}} = 77.78\text{ min}$$

$$t_{1/2} = 77.78\text{ min}$$

20. The given reaction is a first order . So,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}$$

Using the equation for first order,

$$t = \frac{2.303}{k}\log\frac{C_0}{C_t} \quad \text{...(i)}$$

Let $C_0 = 1$ and $C_t = \frac{3}{10}$

So, $$\frac{C_0}{C_t} = \frac{1}{\frac{3}{10}} = \frac{10}{3}$$

Putting values in Eq. (i),

$$t = \frac{2.303}{0.693}\times 5730\ \log\frac{10}{3}$$

$$t = 19042\times(1 - 0.4771) = 9957\text{ years}$$

21. (i) $t_{1/2} = \dfrac{0.693}{200\text{ s}^{-1}} = 0.346\times10^{-2}\text{s} = 3.46\times10^{-3}\text{s}$

(ii) $t_{1/2} = \dfrac{0.693}{2\text{ min}^{-1}} = 0.346\text{ min} = 3.46\times10^{-1}\text{min}$

(iii) $t_{1/2} = \dfrac{0.693}{4\text{ yr}^{-1}} = 0.173\text{ yr} = 1.73\times10^{-1}\text{yr}$

22. For a first order reaction,

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

When a first order reaction is 25% complete in 20 min.

$a = 100$, $a - x = 100 - 25 = 75$, $t = 20$ min.

$$\therefore\quad k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{20}\log\frac{100}{75}$$

$$= \frac{2.303}{20}[\log 4 - \log 3] = 0.0143\text{ min}^{-1}$$

For 75% completion of reaction,

$a = 100$, $a - x = 100 - 75 = 25$, $k = 0.0143\text{ min}^{-1}$

$$t = \frac{2.303}{k}\log\frac{a}{a-x} = \frac{2.303}{0.0143}\log\frac{100}{25}$$

$$= \frac{2.303}{0.0143}\log 4 = 96.961\text{ min.}$$

23. $C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$

Initial pressure at $t = 0$, 0.30 atm

After 300s, $p_{\text{total}} = 0.30 - p + p + p$ atm

$= 0.30 + p$ atm

p_{total} (given) $= 0.50 = 0.30 + p$

$\Rightarrow \quad p = 0.50 - 0.30\text{ atm} = 0.20\text{ atm}$

Pressure of $C_2H_5Cl(g)$ after 300 sec

$(p_{C_2H_5Cl}) = 0.30 - 0.20\text{ atm} = 0.10\text{ atm}$

$$k = \frac{2.303}{t}\log\frac{(p_{C_2H_5Cl})_0}{(p_{C_2H_5Cl})_{300}} = \frac{2.303}{300}\log\frac{0.30\text{atm}}{0.10\text{atm}}$$

$$= \frac{2.303}{300}\log 3 = \frac{2.303}{300}\times 0.4771 = 3.66\times10^{-3}\text{s}^{-1}$$

24. $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$

	$SO_2Cl_2(g)$	$SO_2(g)$	$Cl_2(g)$
Initial pressure	p_i	0	0
After time, t	$p_i - p$	p	p

Total pressure after time t,

i.e. $\quad p_t = p_i - p + p + p = p_i + p$

$\Rightarrow \quad p = p_t - p_i$

Thus, $a = p_i$ and $a - x = p_i - p = p_i - (p_t - p_i)$

$= p_i - p_t + p_i = 2p_i - p_t$

Substituting the values of a and $(a - x)$ in equation,

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$k = \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)}$$

Calculation of rate constant (k), when $t = 100$s

Given, $p_i = 0.4$ atm and $p_t = 0.7$ atm

Then, $$k = \frac{2.303}{100}\log\frac{p_i}{(2p_i - p_t)}$$

$$= \frac{2.303}{100}\log\frac{0.4}{(2\times0.4 - 0.7)}$$

$$= \frac{2.303}{100}\log\frac{0.4}{0.1} = \frac{2.303}{100}\log 4$$

$$= \frac{2.303}{100}\times 0.6021 = 0.01387 = 1.387\times10^{-2}\text{s}^{-1}$$

25. ***Case I*** If $a = 100$, $(a - x) = (100 - 99) = 1$

For 99% completion of the reaction,

$$t_{99\%} = \frac{2.303}{k} \log \frac{100}{1} = \frac{2.303}{k} \log 10^2 = \frac{2.303 \times 2}{k}$$

$$t_{99\%} = \frac{4.606}{k} \quad ...(i)$$

Case II If $a = 100$

$$(a - x) = (100 - 90) = 10$$

For 90% completion of the reaction,

$$t_{90\%} = \frac{2.303}{k} \log \frac{100}{10}$$

$$= \frac{2.303}{k} \log 10 = \frac{2.303}{k} \quad ...(ii)$$

On dividing Eq. (i) by Eq. (ii), we get

$$\frac{t_{99\%}}{t_{90\%}} = \frac{4.606}{k} \times \frac{k}{2.303} = 2$$

It means that time required for 99% completion of the reaction is twice the time required to complete 90% of the reaction.

26. For a first order reaction, $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

$$t = \frac{2.303}{(1.15 \times 10^{-3} s^{-1})} \times \log \frac{(5\text{ g})}{(3\text{ g})}$$

$$= \frac{2.303}{(1.15 \times 10^{-3} s^{-1})} (\log 5 - \log 3)$$

$$= \frac{2.303}{(1.15 \times 10^{-3} s^{-1})} (0.6990 - 0.4771)$$

$$= 2.0 \times 10^3 \times 0.2219\text{ s} = 443.8\text{ s}$$

or time = 444 s

27. For first order reactions,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(3.0\text{ h})}$$

or $$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

or $$\log \frac{[A]_0}{[A]} = \frac{k \times t}{2.303}$$

$$\log \frac{[A]_0}{[A]} = \frac{0.693}{3\text{ h}} \times \frac{8\text{ h}}{2.303} = 0.8024$$

$$\frac{[A]_0}{[A]} = \text{antilog } 0.8024 = 6.345$$

$[A]_0 = 1\text{ M}$; $\quad [A] = \frac{[A]_0}{6.345} = \frac{1\text{ M}}{6.345} = 0.1576\text{ M}$

After 8 h, sucrose left = 0.1576 M

28. When time and rate of a reaction is given then we can use hit and trial method to find out the order of reaction by substituting the values in different integrated equation. Using data, to find out the rate constant.

t/s	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(i) Using hit and trial method,

For first order reaction, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

Here, $t = 300$ s, $[R]_0 = 1.6 \times 10^{-2}$ mol L^{-1} and $[R] = 0.8 \times 10^{-2}$ mol L^{-1}

$$k = \frac{2.303}{300} \log \frac{(1.6 \times 10^{-2})\text{ mol L}^{-1}}{(0.8 \times 10^{-2})\text{ mol L}^{-1}}$$

$$= \frac{2.303}{300} \log 2 = \frac{2.303}{300} \times 0.3010$$

$$k = 2.31 \times 10^{-3}\text{ s}^{-1}$$

Similarly, $$k = \frac{2.303}{600} \log \frac{(1.6 \times 10^{-2})\text{ mol L}^{-1}}{(0.4 \times 10^{-2})\text{ mol L}^{-1}}$$

$$k = 2.31 \times 10^{-3}\text{ s}^{-1}$$

Thus, it is proved that reaction proceed through first order kinetics as the rate constant remains same.

(ii) Half-life $(t_{1/2}) = \frac{0.693}{k}$

$$t_{1/2} = \frac{0.693}{2.31 \times 10^{-3}}\text{ s}^{-1}$$

$$t_{1/2} = 300\text{ s}$$

29. For first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

The given first order reaction 25% completes in 40 min.

Let, $a = 100$

$$a - x = 100 - 25$$

$$a - x = 75$$

$\therefore$ $$k = \frac{2.303}{40} \log \frac{100}{75} = \frac{2.303}{40} (\log 4 - \log 3)$$

$$k = 0.0072\text{ min}^{-1}$$

For 80% completion of reaction,

$$a = 100$$

$$a - x = 100 - 80 = 20$$

$$K = 0.0072\text{ min}^{-1}$$

$$t = \frac{2.303}{0.0072} \log \frac{100}{20}$$

$$t = 223.6\text{ min}$$

30. Let the pressure of a azoisopropane decreases by x atm. As 1 mole of azoisopropane decompose to give 1 mole of N_2 and 1 mole of hexane (C_6H_{14}), the pressure of N_2 and hexane increases by x atm.

$$\underset{\text{Azoisopropane}}{(CH_3)_2CHN{=}NCH(CH_3)_2(g)} \longrightarrow N_2(g) + C_6H_{14}(g)$$

	Azoisopropane	N_2	C_6H_{14}
At $t = 0$	35.0 atm	0 atm	0 atm
At time, t	$(35.0 - x)$ atm	x atm	x atm

$$p_t = p_{\text{azoisopropane}} + p_{N_2} + p_{C_6H_{14}}$$

$$p_t = 35.0 - x + x + x$$

$$p_t = 35 + x$$

$\Rightarrow$ $$x = p_t - 35$$

$\therefore$ $$p_{\text{azoisopropane}} = 35.0 - (p_t - 35) = 70 - p_t$$

(i) Rate constant after 360 s $= k_1$

At $t = 360$ s, $p_i = 35$ atm

$p_t = 54$ atm

$\therefore$ $p_{azoisopropane} = (70 - 54)$ atm $= 16$ atm

$\therefore$ Rate constant, k_1

$$= \frac{2.303}{360} \log \frac{35}{16} = \frac{2.303}{360} \log 2.187$$

$$= \frac{2.303 \times 0.33984}{360} = 2.17 \times 10^{-3} s^{-1}$$

(ii) Rate constant after 720s, k_2

$p_i = 35$ atm, $p_t = 63.0$ atm

$\therefore$ $p_{azoisopropane} = (70 - 63)$ atm $= 7$ atm

$\therefore$ Rate constant,

$$k_2 = \frac{2.303}{720} \log \frac{35}{7} = \frac{2.303}{720} \log 5 = \frac{2.303 \times 0.6990}{720}$$

$$= 2.24 \times 10^{-3} \text{ s}^{-1}$$

Average rate constant,

$$k = \frac{(2.17 + 2.24)}{2} \times 10^{-3}$$

$$= 2.21 \times 10^{-3} \text{ s}^{-1}$$

31. $t_{1/2} = 28.1$ yr, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1}$ yr^{-1}

For first order reaction,

$$t = \frac{2.303}{k} \log \frac{a}{(a-x)}$$

Case I

$a = 1\ \mu$g, $t = 10$yr, $k = \frac{0.693}{28.1}$ yr^{-1}

$$10 \text{ yr} = \frac{2.303}{0.693} \times 28.1 \text{ yr} \log \frac{a}{(a-x)}$$

$$\log \frac{a}{(a-x)} = \frac{10 \text{ yr} \times 0.693}{2.303 \times 28.1} = 0.107$$

$$\frac{a}{(a-x)} = \text{antilog}(0.107) = 1.279$$

$$(a-x) = \frac{a}{1.279} = \frac{(1\ \mu\text{g})}{1.279} = 0.7819\ \mu\text{g}$$

Amount left after 10 yr $= 0.7819\ \mu$g **(1)**

Case II $a = 1\ \mu$g, $t = 60$ yr

$$k = \frac{0.693}{28.1} \text{ yr}^{-1}$$

$$60 \text{ yr} = \frac{2.303}{0.693/28.1 \text{ yr}^{-1}} \times \log \frac{a}{(a-x)}$$

$$\log \frac{a}{(a-x)} = \frac{(60 \text{ yr}) \times 0.693/28.1 \text{ yr}^{-1}}{2.303} = 0.642$$

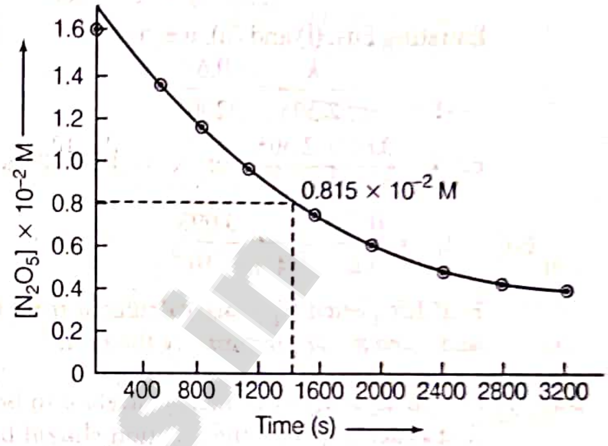
$$\frac{a}{(a-x)} = \text{antilog } 0.642 = 4.385$$

$$(a-x) = \frac{a}{4.385}$$

$$= \frac{(1\ \mu\text{g})}{4.385} = 0.2280\ \mu\text{g}$$

Amount left after 60 yr $= 0.2280\ \mu$g **(1)**

32. (i) The plot of $[N_2O_5]$ against time is shown below :



(ii) Initial concentration [at $t = 0$] of N_2O_5

$$= 1.63 \times 10^{-2} \text{ M}$$

Half of its concentration $= \frac{1.63 \times 10^{-2}}{2}$

$$= 0.815 \times 10^{-2} \text{ M}$$

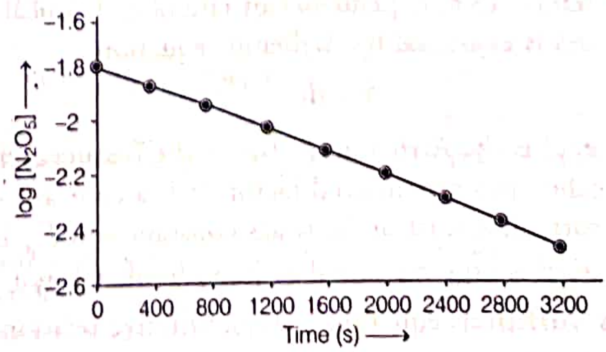
From, the above graph, the time which corresponds to 0.815×10^{-2} M concentration is 1450 s.

Hence, $t_{1/2} = 1450$ s

(iii)

t/s	$10^{-2} \times [N_2O_5]$ / mol L^{-1}	$\log [N_2O_5]$
0	1.63	− 1.79
400	1.36	− 1.87
800	1.14	− 1.94
1200	0.93	− 2.03
1600	0.78	− 2.11
2000	0.64	− 2.19
2400	0.53	− 2.28
2800	0.43	− 2.37
3200	0.35	− 2.46

The plot of $\log [N_2O_5]$ and time can be represented as :



(iv) As the plot of $\log[N_2O_5]$ *versus* time obtained is a straight line, hence it is a reaction of first order,

$\therefore$ Rate $= k[N_2O_5]$

(v) For first order reaction, the slope of the line

$$= -\frac{k}{2.303} \quad \text{...(i)}$$

$$\therefore \quad \text{Slope} = \frac{-2.46-(-1.79)}{3200-0} = \frac{-0.67}{3200} \quad \text{...(ii)}$$

Equating Eqs. (i) and (ii), we get

$$-\frac{k}{2.303} = \frac{-0.67}{3200}$$

$$\text{or} \quad k = \frac{0.67 \times 2.303}{3200} \quad \text{or} \quad k = 4.82 \times 10^{-4}\,s^{-1}$$

(vi) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.82 \times 10^{-4}\,s^{-1}} = 1438\,s$

Half-life period ($t_{1/2}$) are calculated from the formula and slope are approximately the same.

33. (i) For the hydrolysis of methyl acetate to be pseudo first order reaction, the reaction should be first order with respect to ester when (H_2O) is constant.

The rate constant, k for pseudo first order reaction is

$$k = \frac{2.303}{t} \log \frac{[C]_0}{[C]},$$

where, $k = k'[H_2O]$

where, $[C]_0$ and $[C]$ are initial and final concentration of the reactant, respectively.

$$\text{At } t_1 = 30s, \; k_1 = \frac{2.303}{30} \log \frac{0.60}{0.30} = 2.3 \times 10^{-2} s^{-1}$$

At $t_2 = 60s$,

$$k_1 = \frac{2.303}{60} \log \frac{0.60}{0.15} = 2.3 \times 10^{-2} s^{-1}$$

It can be seen that the rate constant, k, i.e. $k'[H_2O]$ for the reaction has a constant value and equal to $2.3 \times 10^{-2}\,s^{-1}$. Hence, the given reaction is pseudo first order reaction.

(ii) Average rate during interval 30 – 60s

$$\frac{C_2 - C_1}{t_2 - t_1} = \frac{0.30 - 0.15}{60 - 30} \text{mol L}^{-1} s^{-1} = 0.005 \text{ mol L}^{-1} s^{-1}$$

|TOPIC 4|
Temperature Dependence of the Rate of a Reaction

Most of the chemical reactions are accelerated by increase in temperature.

It has been found that **for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.** e.g. In decomposition of N_2O_5, the time taken for half of the original amount to decompose is 12 min at 50°C, 5 h at 25°C and 10 days at 0°C. The effect of temperature is usually expressed in terms of **temperature coefficient.**

ARRHENIUS EQUATION

The temperature dependence of rate of a chemical reaction is expressed by Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

where, A is the Arrhenius factor or the frequency factor, also called **pre-exponential** factor. It is a constant specific to a particular reaction. R is gas constant and E_a is the activation energy measured in joules/mole (J mol^{-1}).

Thus, Arrhenius equation is a quantitative relationship between rate constant and temperature.

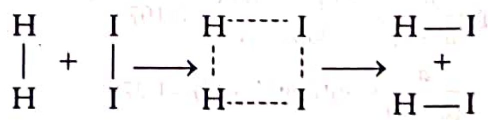
Note The temperature dependence of the rate of a chemical reaction was first proposed by J.H. van't Hoff but Arrhenius provided its physical justification and interpretation.

ARRHENIUS THEORY

It explains that the products are formed through the intermediates or activated complex.

This can be understand by the following reaction :

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$



Intermediate

Formation of HI through the intermediate

According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate. It exists for a very short time and then breaks to form two molecules of hydrogen iodide.

Activation Energy (E_a)

The energy needed to form the intermediate [called **activated complex** (C)] is known as activation energy (E_a). It is the extra energy required by the reactant molecules that results into effective collision between them to form the products.

Some energy is released when the activated complex decomposes to form products. Therefore, the final enthalpy of the reaction depends upon the nature of reactants and products.

To convert reactants into products they have to cross an energy barrier (also called potential barrier) and achieve the threshold energy as shown in the figure, which has been obtained by plotting potential energy *versus* reaction coordinate.

Reaction coordinate represents the profile of energy change, when reactants change into products. Here, we have taken example of formation of HI from H_2 and I_2 molecules.

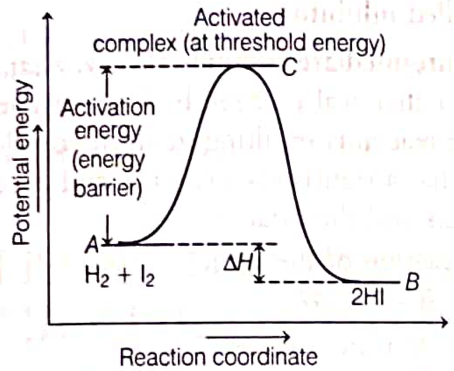


Figure showing plot of potential energy *versus* reaction coordinate

Note (i) Threshold energy is the minimum energy which the colliding molecules must have for effective collision.
(ii) Effective collisions are those collisions which lead to the formation of product molecules.

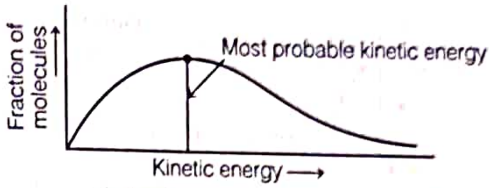
MAXWELL BOLTZMANN DISTRIBUTION CURVE

At a particular temperature T, all the molecules of reactants do not have the same kinetic energy but the fractions of molecules having particular kinetic energies at a particular temperature remain constant.

The distribution of kinetic energy may be described by plotting the fraction of molecules (N_E/N_T) with a given kinetic energy (E). This is called Maxwell's distribution of energies. Here, N_E is the number of molecules with energy E and N_T is the total number of molecules.

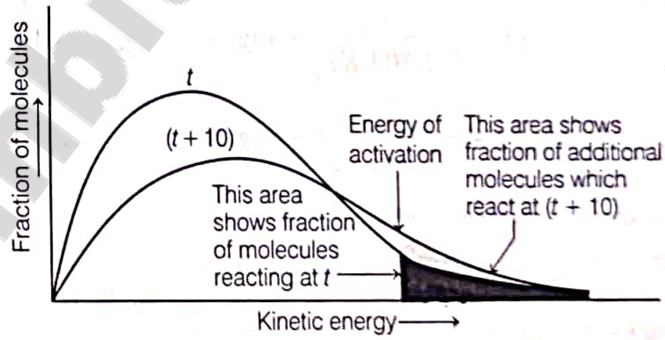
The peak of the curve represents the kinetic energy possessed by the maximum fraction of molecules, that is known as **most probable kinetic energy**. Very less number of molecules possess either very low or very high kinetic energy.

Most of the molecules have average or intermediate kinetic energies between the most probable kinetic energy and the lowest kinetic energy.



Distribution curve showing energies among gaseous molecules

On raising temperature to $t + 10$, the maximum of the curve shifts to higher kinetic energy value and the curve spreads to the right such that there is a greater proportion of molecules with much higher energies. However, the total area under the curve must be constant, since total probability must be one at all times. We can easily mark and determine E_a (activation energy) with the Maxwell Boltzmann distribution curve.



Distribution curve showing temperature dependence of rate of a reaction

Rise in temperature of the substance increases the fraction of molecules that collides with energies more than E_a.

The graph shows that in the curve at $(t + 10)$ the area showing the fraction of reacting molecules having energy equal to or greater than activation energy gets doubled and hence, double the rate of a reaction.

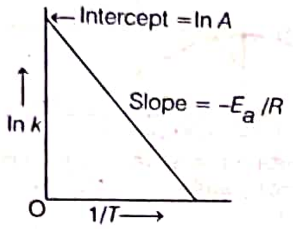
In Arrhenius equation, $k = Ae^{-E_a/RT}$, the factor $e^{-E_a/RT}$ represents the fraction of molecules that have kinetic energy more than the activation energy (E_a). Thus, it is clear from Arrhenius equation that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

Taking natural logarithm on both sides, the Arrhenius equation becomes,

$$\ln k = -\frac{E_a}{RT} + \ln A$$

The plot of $\ln k$ *versus* $1/T$ gives a straight line.

Slope of this plot gives the value of $-\frac{E_a}{R}$ and the intercept gives the value of ln A.



A plot between ln k and $1/T$

E_a and A can also be determined from the rate constants at two different temperatures.

$$\ln k = -\frac{E_a}{RT} + \ln A \quad \text{or} \quad \log k = -\frac{E_a}{2.303\ RT} + \log A$$

Let k_1 and k_2 be the rate constants at temperatures T_1 and T_2. Then,

$$\log k_1 = -\frac{E_a}{2.303\ RT_1} + \log A \quad \text{...(i)}$$

$$\log k_2 = -\frac{E_a}{2.303\ RT_2} + \log A \quad \text{...(ii)}$$

A = constant for the given reactions.

Subtracting Eq. (i) from Eq. (ii), we have

$$\log k_2 - \log k_1 = \frac{E_a}{2.303\ RT_1} - \frac{E_a}{2.303\ RT_2}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\boxed{\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]}$$

EXAMPLE |1| **The decomposition of hydrocarbon follows the equation, $k = (4.5\times 10^{11}\ s^{-1})\,e^{-28000\ K/T}$. Calculate E_a.** **NCERT**

Sol. According to Arrhenius equation, $k = Ae^{-E_a/RT}$ ...(i)

According to the available data

$$k = (4.5\times 10^{11}\ s^{-1})\,e^{-28000\ K/T} \quad \text{...(ii)}$$

On comparing both equations, we have

$$-\frac{E_a}{RT} = \frac{-28000\ K}{T}$$

$$E_a = (28000\ K)\times R = (28000\ K)\times(8.314\ K^{-1} J\ mol^{-1})$$

$$= 232792\ J\ mol^{-1}$$

$$E_a = 232.792\ kJ\ mol^{-1}$$

EFFECT OF CATALYST

A **catalyst** is a substance which increases the rate of reaction without itself undergoing any permanent chemical change, e.g. hydrogen and oxygen do not react at room temperature but in the presence of spongy or powder platinum, the reaction occurs vigorously. Similarly, MnO_2 catalyses the following reaction in the order to raise its rate considerably.

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

The word catalyst should not be used when the added substances reduces the rate of reaction. In such cases, the substance is called **inhibitor**.

According to **intermediate complex theory**, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transistory existence and decomposes to yield products and the catalyst.

For a general reaction of the type,

$$A + B \longrightarrow AB$$

Uncatalysed reaction proceed as:

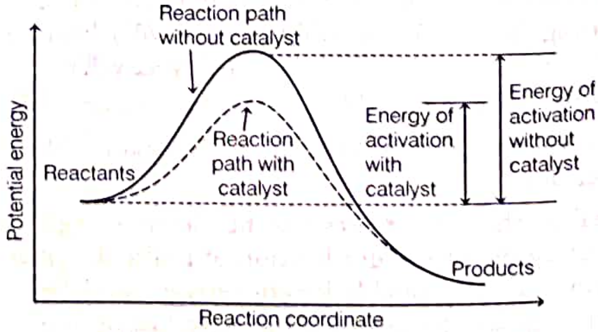
$$A + B \longrightarrow [A-B] \longrightarrow \underset{\text{Product}}{AB}$$

Catalysed reaction proceed as:

$$\underset{\text{Reactants}}{A + B} + \underset{\text{Catalyst}}{C} \longrightarrow \underset{\text{Intermediate complex}}{ABC} \rightarrow \underset{\text{Product}}{A—B} + \underset{\text{Catalyst regenerated}}{C}$$

Since, the catalyst is regenerated after the decomposition of the intermediate so, a small amount of catalyst is enough for a large amount of reactants.

It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products, hence lowering the potential energy barrier as shown in the figure. It is also clear from the Arrhenius equation ($k = Ae^{-E_a/RT}$) that lower the value of E_a faster will be the rate of reaction.



Effect of catalyst on activation energy

Characteristics of a Catalyst

(i) A small amount of the catalyst can catalyse a large amount of reactions.

(ii) A catalyst does not alter Gibbs energy, ΔG of a reaction.

(iii) It does not change the equilibrium constant rather it helps in attaining the equilibrium faster, i.e. it catalyses the forward and backward reactions both to the same extent so that the equilibrium state remains same but is reached earlier.

(iv) A catalyst catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.

(v) A catalyst is highly specific. They have an ability to direct the reaction to yield a particular product. The reaction with same reactants but different catalyst may yield different products.

(vi) A catalyst never starts a reaction which has no tendency to proceed.

COLLISION THEORY OF CHEMICAL REACTIONS

Although Arrhenius equation is applicable under a wide range of circumstances, yet collision theory, developed by **Max Trautz** and **William Lewis** in 1916-18, provides a greater insight into the energetic and mechanistic aspects of reactions. Collision theory is based on kinetic theory of gases.

According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. **The number of collisions per second per unit volume of the reaction mixture is called collision frequency** (Z). E_a is another factor which affects the rate of chemical reactions. For a bimolecular elementary reactions,

$$A + B \longrightarrow \text{Products}$$

Rate of reaction can be expressed as:

$$\text{Rate} = Z_{AB}\, e^{-E_a/RT}$$

where, Z_{AB} is the collision frequency of the reactants A and B and $e^{-E_a/RT}$ is the fraction of molecules with energies equal to or greater than E_a.

When Arrhenius equation, $k = Ae^{-E_a/RT}$ is compared to the above equation, A can be related to the **collision frequency** (Z).

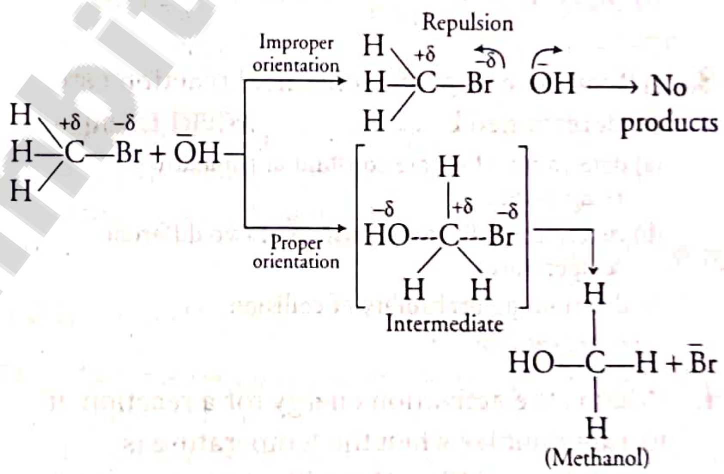
Not all the collisions result into product. Collisions in which molecules have sufficient kinetic energy (which is also called **threshold energy**) and proper orientation result into breaking of bond between the reacting species and formation of new bonds to form products. These collisions are referred to as the **effective collisions**.

Note Threshold energy = activation energy + energy possessed by reacting species

On the other hand, collisions with improper orientation make the molecules bounce back leading to the formation of no products.

e.g. Formation of methanol from bromomethane depends upon the orientation of reactant molecules.

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$



Proper and improper orientations of colliding molecules

When the orientation factor is taken into account, the expression becomes

$$\text{Reaction rate} = PZ_{AB}\, e^{-E_a/RT}$$

where, P is orientation factor or steric factor or probability factor. It takes into account the fact that in a collision, molecules must be properly oriented.

Therefore, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and thus, the rate of a chemical reaction.

Limitation of Collision Theory

This theory explains the results of a number of reactions but it does not give satisfactory explanation in some cases as it considers atoms/molecules to be hard spheres and ignores their structural aspect.

TOPIC PRACTICE 4

OBJECTIVE Type Questions

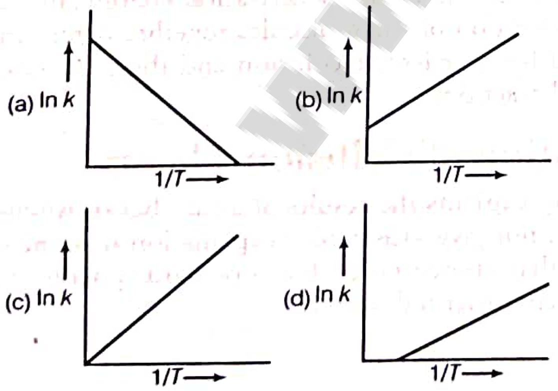
1. The temperature coefficient of a reaction is
(a) the ratio of rate constant at two temperatures
(b) the ratio of rate constant differing by 10° preferably 25°C and 35°C
(c) the rate constant at a fixed temperature
(d) None of the above

2. Arrhenius equation may not be represented as
(a) $\ln \frac{A}{k} = \frac{E_a}{RT}$ (b) $k = Ae^{-Ea/RT}$
(c) $\log A = \log k + \frac{E_a}{2.303RT}$ (d) $\log k - \left(\frac{E_a}{RT}\right) = A$

3. Activation energy of a chemical reaction can be determined by .... **NCERT Exemplar**
(a) determining the rate constant at standard temperature
(b) determining the rate constant at two different temperatures
(c) determining probability of collision
(d) using catalyst

4. What is the activation energy for a reaction, if its rate doubles when the temperature is raised from 20°C to 35°C? ($R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$)
(a) 342 kJ mol^{-1} (b) 269 kJ mol^{-1}
(c) 34.7 kJ mol^{-1} (d) 15.1 kJ mol^{-1}

5. According to Arrhenius equation rate constant k is equal to $A\,e^{-E_a/RT}$. Which of the following options represents the graph of $\ln k$ vs $\frac{1}{T}$? **NCERT Exemplar**



6. The role of a catalyst is to change .... **NCERT Exemplar**
(a) Gibbs energy of reaction
(b) enthalpy of reaction
(c) activation energy of reaction
(d) equilibrium constant

7. In the presence of a catalyst, the heat evolved or absorbed during the reaction .... **NCERT Exemplar**
(a) increases
(b) decreases
(c) remains unchanged
(d) may increase or decrease

8. After introducing the factor P, expression for the rate of a reaction, becomes
(a) Rate $= \frac{Z_{AB}e^{-E_a/RT}}{P}$ (b) Rate $= PZ_{AB}\, e^{-E_a/RT}$
(c) Rate $= \frac{Z_{AB} \cdot P}{e^{E_a/RT}}$ (d) Rate $= \frac{e^{E_a/RT}}{PZ_{AB}}$

VERY SHORT ANSWER Type Questions

9. Why a reaction does not have a zero activation energy?

10. Oxygen is available in plenty in air yet fuels do not burn by themselves at room temperature. Explain. **NCERT Exemplar**

11. What is the effect of adding a catalyst on
(i) Activation energy (E_a) and
(ii) Gibbs energy (ΔG) of a reaction? **All India 2017**

12. Why in redox titration of $KMnO_4$ *versus* oxalic acid, we heat oxalic acid solution before starting the titration? **NCERT Exemplar**

13. Why equilibrium constant remain unchanged in the presence of a catalyst?

14. In some case, it is found that a large number of colliding molecules have energy more than threshold energy, yet the reaction is slow. Why? **Delhi 2013; NCERT Exemplar**

SHORT ANSWER Type I Questions

15. What is the effect of temperature on the rate constant of a reaction? How can this effect of temperature on rate constant be represented quantitatively? **NCERT**

16. (i) Explain why H_2 and O_2 do not react at room temperatue.
(ii) Write the rate equation for the reaction, $A_2 + 3B_2 \longrightarrow 2C$, if the overall order of the reaction is zero. **All India 2017 C**

17. (a) A first order reaction is 50% complete in 30 min at 300 K and in 10 minutes at 320 K. Calculate activation energy (E_a) for the reaction. ($R = 8.314$ JK^{-1} mol^{-1})
(b) Write the two conditions for collisions to be effective collisions. **Delhi 2020**

SHORT ANSWER Type II Questions

18. The activation energy for the reaction, $2HI(g) \longrightarrow H_2(g) + I_2(g)$ is 209.5 kJ mol^{-1} at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy. **NCERT Intext**

19. The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of the activation (E_a) of the reaction assuming that it does not change with temperature. [$R = 8.314$ JK^{-1} mol^{-1}, $\log 4 = 0.6021$] **All India 2013; NCERT**

20. The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E_a. **NCERT Intext**

Or

The rate of most reactions become double when their temperature is raised from 298 K to 308 K. Calculate their activation energy.

(Given, $R = 8.314$ J mol K^{-1})

21. The rate constant for the decomposition of hydrocarbons is 2.418×10^{-5} s^{-1} at 546 K. If the energy of activation is 179.9 kJ mol^{-1}, what will be the value of pre-exponential factor? **NCERT**

22. The decomposition of A into product has value of k as 4.5×10^3 s^{-1} at 10°C and energy of activation 60 kJ mol^{-1}. At what temperature would k be 1.5×10^4 s^{-1}? **NCERT; Delhi 2013**

23. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} \text{K}$$

Calculate E_a for this reaction and rate constant k if its half-life period be 200 min.
(Given, $R = 8.314$ JK^{-1}mol^{-1}) **Delhi 2016**

24. The rate of reaction quadruples when temperature changes from 293 K to 313 K. Calculate E_a assuming that it does not change with time. [$R = 8.314$ JK^{-1}mol^{-1}] **All India 2019**

25. Draw the plot of $\ln k$ vs $1/T$ for a chemical reaction. What does the intercept represent? What is the relation between slope and E_a? **All India 2019**

LONG ANSWER Type Questions

26. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of A is 4×10^{10} s^{-1}. Calculate k at 318 K and E_a. **NCERT**

27. The rate constant for the decomposition of N_2O_5 at various temperatures is given below.

T/°C	0	20	40	60	80
$10^5 \times K/s^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between $\ln k$ and $1/T$ and calculate the values of A and E_a. Predict the rate constant at 30°C and 50°C. **NCERT**

HINTS AND EXPLANATIONS

1. (*b*) The temperature coefficient of a reaction is the ratio of rate constant differing by 10° preferably 25°C and 35°C.

2. (*d*) Arrhenius equation is

$$k = Ae^{-E_a/RT}$$

On taking ln

$$\ln k = \ln A + \left(-\frac{E_a}{RT}\right)$$

Or $\log A - \log k = \frac{E_a}{2.303\,RT}$ or $\log A = \log k + \frac{E_a}{2.303\,RT}$

3. (*b*) Activation energy of a chemical reaction is related to rate constant of a reaction at two different temperatures, i.e. k_1 and k_2 respectively

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

This equation is known as Arrhenius equation.

4. (*c*) Given, initial temperature

$$T_1 = 20 + 273 = 293\text{ K}$$

Final temperature, $T_2 = 35 + 273 = 308$ K

$$R = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$$

As rate constant, $k \propto r \Rightarrow \frac{k_2}{k_1} = 2$

From Arrhenius equation, we know that

$$\log\frac{k_2}{k_1} = -\frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log 2 = -\frac{E_a}{2.303 \times 8.314}\left[\frac{308 - 293}{293 \times 308}\right]$$

$$E_a = 34673.48\text{ J mol}^{-1} = 34.7\text{ kJ mol}^{-1}$$

5. (*a*) According to Arrhenius equation, $k = A\,e^{-E_a/RT}$

Taking log on both side $\ln k = \ln\,(A.e^{-\frac{E_a}{RT}})$

On comparing with equation of straight line, graph 'a' represents the graph of $\ln k$ *vs* $\frac{1}{T}$.

6. (*c*) The role of a catalyst is to change the activation energy of reaction. This is done by either increasing or decreasing activation energy of molecule as catalyst are mainly of two types; +ve catalyst and –ve catalyst.

7. (*c*) In the presence of catalyst, the heat absorbed, or evolved during the reaction remains unchanged as there is no change in stability of reactant and product.

8. (*b*) After introducing the factor *P*, expression for the rate of reaction becomes $PZ_{AB}e^{-E_a/RT}$.

9. According to Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

If $E_a = 0$, $k = A$, i.e. rate constant equals to collision frequency which suggests that every collision results into a chemical reaction that cannot be true. Hence, $E_a \neq 0$.

10. The activation energy for the combustion of fuels is very high at room temperature.

11. (i) Catalyst lowers the activation energy and changes the path of the reaction.
(ii) A catalyst does not alter Gibbs energy (ΔG) of a reaction.

12. On increasing the temperature, the rate of reaction increases. Thus, on heating the oxalic acid solution before titration, the rate of decolourisation becomes fast and hence, rate of reaction increases.

13. It catalyses the forward and backward reactions to the same extent so that the equilibrium state remains same.

14. It is due to improper orientation of reacting molecules.

15. Refer to the text on page 118 and 119.
[**Hint** On increasing the temperature to 10°C, i.e. $t + 10$, the rate of reaction become doubled.]

16. (i) The activation energy for the reaction of H_2 with O_2 is very high at room temperature.
(ii) In zero order reaction, the rates does not depend on the concentration of any of the reactants.
Thus, overall order is zero.
$\therefore$ Rate $= k[A]^0[B]^0$.

17. (a) Refer to page 125 (Sol. 20).
[*Ans.* $E_a = 43.84$ kJ mol^{-1}]
(b) Refer to page 121 (Collision theory of chemical reactions).

18. For the given reaction, $E_a = 209.5$ kJ mol^{-1}
$= 209500$ J mol^{-1}

$$T = 581\text{ K},\ R = 8.314\text{ JK}^{-1}\text{mol}^{-1}$$

The fraction of molecules having energy equal to or greater than E_a is $x = e^{-E_a/RT}$.

$$\therefore \ln x = -E_a/RT$$

$$\log x = -\frac{E_a}{2.303\,RT}$$

$$= -\frac{209500\text{ J mol}^{-1}}{2.303 \times 8.314\text{ JK}^{-1}\text{ mol}^{-1} \times 581\text{ K}} = -18.8323$$

$$x = \text{antilog}\,(-18.8323)$$

$$x = 1.471 \times 10^{-19}$$

19. Given, $T_1 = 293$ K, $T_2 = 313$ K, $k_2/k_1 = 4$,
$R = 8.314$ JK^{-1} mol^{-1}, log4 = 0.6021

We know, $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

$$\therefore \quad \log 4 = \frac{E_a}{2.303 \times 8.314}\left[\frac{313-293}{313 \times 293}\right]$$

$$\Rightarrow \quad 0.6021 = \frac{E_a}{19.147}\left[\frac{20}{91709}\right]$$

$$\Rightarrow \quad E_a = \frac{0.6021 \times 19.147 \times 91709}{20}$$

$$\Rightarrow \quad E_a = 52862.94 \text{ J mol}^{-1}$$

20. According to Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\frac{k_2}{k_1} = 2, T_1 = 298 \text{ K}, T_2 = 308 \text{ K}, R = 8.314 \text{ JK}^{-1}\text{ mol}^{-1}$$

$$\log 2 = \frac{E_a}{2.303 \times (8.314 \text{ JK}^{-1}\text{mol}^{-1})}\left[\frac{1}{298\text{K}} - \frac{1}{308\text{K}}\right]$$

$$\text{or } 0.3010 = \frac{E_a}{2.303 \times (8.314 \text{ J mol}^{-1})} \times \frac{10}{298 \times 308}$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 298 \times 308}{10}(\text{J mol}^{-1})$$

$$= 52897.78 \text{ J mol}^{-1}$$

$$= 52.898 \text{ kJ mol}^{-1}$$

Activation energy for the reaction = $52.898 \text{ kJ mol}^{-1}$

21. According to Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303RT}$$

We have, $k = 2.418 \times 10^{-5}\text{s}^{-1}$;

$$E_a = 179.9 \text{ kJ mol}^{-1} \text{ or } 179900 \text{ J mol}^{-1};$$

$$R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}; \quad T = 546 \text{ K}$$

$$\Rightarrow \quad \log A = \log k + \frac{E_a}{2.303RT}$$

$$= \log(2.418 \times 10^{-5}\text{s}^{-1}) + \frac{179900 \text{ J mol}^{-1}}{2.303 \times (8.314 \text{ JK}^{-1}\text{mol}^{-1}) \times 546 \text{ K}}$$

$$\log A = -4.6184 + 17.21 = 12.5916$$

$$A = \text{antilog } 12.5916 = 3.9 \times 10^{12}\text{s}^{-1}$$

22. According to Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \times \frac{T_2 - T_1}{T_1 T_2}$$

$$k_1 = 4.5 \times 10^3 \text{ s}^{-1}$$

$$\Rightarrow \quad k_2 = 1.5 \times 10^4 \text{ s}^{-1};$$

$$T_1 = 10°\text{C}$$

$$= 283 \text{ K} \log \frac{1.5 \times 10^4}{4.5 \times 10^3}$$

$$= \frac{(60000 \text{ J mol}^{-1})}{2.303 \times (8.314 \text{ JK}^{-1}\text{mol}^{-1})}\left(\frac{T_2 - 283}{283 T_2}\right)$$

$$\log 3.333 = 3133.62\left(\frac{T_2 - 283}{283 T_2}\right)$$

$$\Rightarrow \quad \frac{0.5228}{3133.63} = \frac{T_2 - 283}{283 T_2}$$

$$\Rightarrow \quad \frac{0.5228 \times 283}{3133.63} = \frac{T_2 - 283}{T_2}$$

$$\Rightarrow \quad 1 - \frac{283}{T_2} = 0.04721$$

$$\text{or} \quad T_2 = \frac{283}{1 - 0.04721} = \frac{283}{0.95279}$$

$$T_2 = 297.34 \text{ K}$$

$$= (297.02 - 273.0) = 24.34° \text{C}$$

Temperature $= 24.34°$ C

23. According to Arrhenius equation, $k = Ae^{-E_a/RT}$

$$\log k = \log A - \frac{E_a}{2.303 RT} \quad \text{...(i)}$$

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T}\text{K} \quad \text{...(ii)}$$

On comparing Eqs. (i) and (ii)

$$\frac{E_a}{2.303 RT} = \frac{1.0 \times 10^4}{T}\text{K}$$

$$E_a = 2.303R \times 1.0 \times 10^4 \text{K}$$

$$= 2.303 \times 1.0 \times 10^4 \text{ K} \times 8.314 \text{ JK}^{-1}\text{ mol}^{-1}$$

$$= 19.14 \times 10^4 \text{J mol}^{-1}$$

$$= 191.4 \text{ kJ mol}^{-1}$$

Now,

Given, $t_{1/2} = 200 \text{ min} = 200 \times 60\text{s}$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{200 \times 60}$$

$$k = 5.775 \times 10^{-5}\text{s}^{-1}$$

24. Given, $T_1 = 293$ K, $T_2 = 313$ K, $k_2/k_1 = 4$,

$R = 8.314 \text{ JK}^{-1}\text{ mol}^{-1}$, $\log 4 = 0.6021$

$$\because \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\therefore \quad \log 4 = \frac{E_a}{2.303 \times 8.314}\left[\frac{313 - 293}{313 \times 293}\right]$$

$$0.6021 = \frac{E_a}{19.147}\left[\frac{20}{91709}\right]$$

$$E_a = \frac{0.6021 \times 19.147 \times 91709}{20}$$

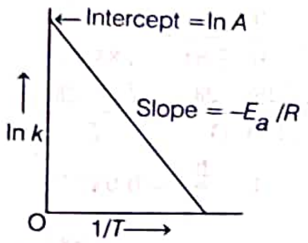
$$= 52862.94 \text{ J mol}^{-1}$$

Hence, $E_a = 52.86294 \text{ kJ mol}^{-1}$

25. The plot of $\ln k$ vs $1/T$ gives a straight line.

Slope of this plot gives the value of $-\frac{E_a}{R}$ and the intercept gives the value of $\ln A$.

E_a and A can also be determined from the rate constants at two different temperatures.



A plot between ln k and $1/T$

26. (i) For first order reaction,

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

At 298 K, $k_1 = \frac{2.303}{t}\log\frac{100}{90}$ ...(i)

At 308 K, $k_2 = \frac{2.303}{t}\log\frac{100}{75}$ ...(ii)

On dividing Eq. (ii) by Eq. (i),

$$\frac{k_2}{k_1} = \frac{\log(100/75)}{\log(100/90)}$$

$$= \frac{0.1249}{0.0458} = 2.73$$

According to Arrhenius theory,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R} \times \frac{T_2 - T_1}{T_1T_2}$$

$$\log 2.73 = \frac{E_a}{2.303\,R}\left[\frac{308-298}{298\times 308}\right]$$

$$E_a = \frac{\left[\begin{array}{r}0.4361\times 2.303\times(8.314\ \text{JK}^{-1}\ \text{mol}^{-1})\\ \times 298\times 308\end{array}\right]}{10}$$

$E_a = 76640\ \text{J mol}^{-1}$

$= 76.640\ \text{kJ mol}^{-1}$

(ii) According to Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

$$\log k = \log(4\times 10^{10}) - \frac{76640\ \text{J mol}^{-1}}{2.303\times(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})\times(318\ \text{K})}$$

$\log k = 10.6021 - 12.5870$

$= -1.9849$

$k = \text{antilog}(-1.9849)$

$= \text{antilog}(\bar{2}.0151)$

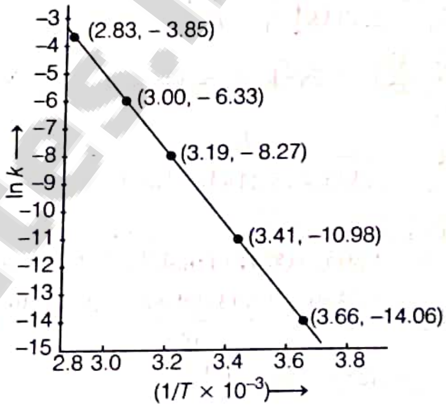
$= 1.035\times 10^{-2}\ \text{s}^{-1}$

So, $E_a = 76.640\ \text{kJ mol}^{-1}$

$k = 1.035\times 10^{-2}\ \text{s}^{-1}$

27. (i) To draw the graph between ln k *versus* $1/T$, we rewrite the data as follows:

T (K)	$1/T$	ln k
273(0°C)	$0.003663 = 3.66\times 10^{-3}$	−14.06
293(20°C)	$0.003413 = 3.41\times 10^{-3}$	−10.98
313(40°C)	$0.003194 = 3.19\times 10^{-3}$	−8.27
333(60°C)	$0.003003 = 3.00\times 10^{-3}$	−6.33
353(80°C)	$0.002833 = 2.83\times 10^{-3}$	−3.85



(ii) From the graph, we find the slope

$$\text{Slope} = \frac{-2.4}{0.00047} = \frac{-E_a}{2.303\,R}$$

∴ Activation energy,

$$E_a = \frac{2.4\times 2.303\times 8.314\ \text{J mol}^{-1}}{0.00047}$$

$= 97772\ \text{J mol}^{-1} = 97.772\ \text{kJ mol}^{-1}$

$\Rightarrow\quad E_a = 97.772\ \text{kJ mol}^{-1}$

(iii) We know that, $\ln k = \ln A + \frac{-E_a}{RT}$

On comparing it with $y = mx + c$. The equation of line in intercept form,

$$\ln k = \left(-\frac{E_a}{R}\right)\frac{1}{T} + \ln A$$

$\log A$ = value of intercept on Y-axis, i.e. on the $\log k$-axis $= (-1 + 7.2) = 6.2$ $\quad [y_2 - y_1 = -1-(7.2)]$

Frequency factor, $A = \text{antilog}\ 6.2 = 1585000$

or, $A = 1.585\times 10^6$ collisions s^{-1}

(iv) Value of rate constant k can be find by the study of graph.

T(K)	$1/T$	Values of $\log K$ from graph	Values of K
303	0.003300	− 4.2	$6.31\times 10^{-5}\text{s}^{-1}$
323	0.003096	− 2.8	$1.585\times 10^{-3}\text{s}^{-1}$

SUMMARY

- The branch of chemistry that deals with the study of the speed or rate of chemical reactions, factors affecting the rates of reaction and the mechanism by which reaction proceed is known as **chemical kinetics.**
- **Rate of reaction** It is the change in the concentration of any one of the reactants or products per unit time. In aqueous reactions, the unit of rate is $molL^{-1}s^{-1}$ while in the case of gaseous reaction, the unit of rate is $atm\,s^{-1}$.
- **Instantaneous rate** It is the rate at a particular instant.

  For $R \to P$ $\quad r_{ins} = -\frac{d[R]}{dt} = +\frac{d[P]}{dt}$
- **Average rate** It is the rate over a long time interval,

$$r_{av} = -\frac{\Delta R}{\Delta t} = +\frac{\Delta P}{\Delta t}$$

- For a reaction, $pA \to qB + rC$

$$\text{rate} = -\frac{d[A]}{p\,dt} = +\frac{d[B]}{q\,dt} = +\frac{d[C]}{r\,dt}$$

  p, q, r = integer of balanced equation.
- **Rate law** It is the expression of rate in terms of molar concentration of reactants.

  For a reaction, $xA + yB \to zC$, Rate $= k[A]^p[B]^q$

  [p and q may or may not be equal to x and y.]
- **Rate constant** (k) It is the rate of chemical reaction when concentration of each reactant is unity. It is also called specific reaction rate. It depends only upon temperature.

  Unit of $k = \left(\frac{\text{mol}}{\text{L}}\right)^{1-n} s^{-1}$ where, [n = order of reaction.]
- **Order of reaction** It is the sum of powers of concentration terms in the rate law expression. It is determined experimentally. e.g. Rate $= k[A]^p[B]^q$, Order $= p + q$
- **Molecularity of reaction** It shows number of species taking part in an elementary (one step) reaction. It never be equal to zero and always a whole number. It has no meaning in complex reaction (reactions involving more than one steps).
- **Zero order reaction** In this reaction, the rate does not depend on the concentration of any of the reactants.

  Rate, $\frac{-d[R]}{dt} = k$ or $kt = [R]_0 - [R]$, $t_{1/2}$ (half-life) $= \frac{R}{2k}$

  Plot of $[R]$ *versus* $[t]$ is a straight line with slope of $-k$ and intercept $[R]_0$.

  First order reaction In this reaction, the rate is proportional to the first power of the concentration of the reactant.

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)} \qquad [a = \text{initial concentration}]$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

  Plot of $[R]_{versus}$ $[t]$ is a straight line with slope of $-k$ and intercept $\ln[R]_0$.

  In terms of pressure, $k = \frac{2.303}{t}\log\frac{p_i}{2p_i - p_t}$
- **Pseudo first order reaction** These reactions are not actually of first order but behave so due to altered conditions. e.g hydrolysis of ester.
- **Temperature coefficient** The effect of temperature is usually expressed in terms of temperature coefficient. For every 10° rise in temperature, the rate becomes double.
- **Arrhenius equation** The temperature dependence of rate of a chemical reaction is expressed as

  $k = Ae^{E_a/RT}$ [where, A = pre-exponential factor, R = gas constant, E_a = activation energy]

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

- **Activation energy** (E_a) It is the energy required by the reactant molecules for effective collision to form products.

  Threshold energy It is the minimum energy which the colliding molecules must have for effective collision.
- **Effect of catalyst** A catalyst increases the rate of reaction by providing a path of lower activation energy. It cannot initiate a reaction, it can only accelerate the rate of reaction. It neither alters free energy change nor enthalpy of the reaction.
- **Collision theory** According to this theory,

$$\text{rate} = Z_{AB}\,e^{-E_a/RT}$$

  where, Z_{AB} = collision frequency

CHAPTER PRACTICE

OBJECTIVE Type Questions

1 For a hypothetical reaction, $R \longrightarrow$ products; rate $= -k[R]$. The negative sign used in the rate expression indicates.

(a) decrease in the concentration of reactants with time
(b) decrease in the rate with time
(c) reaction is reversible
(d) None of the above

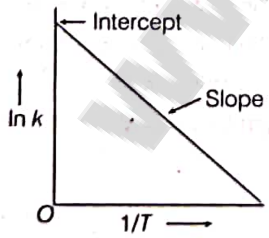
2 A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?

(a) 1.26×10^{15} s
(b) 2.52×10^{14} s
(c) 2.52×10^{28} s
(d) Infinite

3 Which of the following statement is not correct for the catalyst?

(a) It catalyses the forward and backward reactions to the same extent
(b) It alters ΔG of the reaction
(c) It is a substance that does not change the equilibrium constant of a reaction
(d) It provides an alternate mechanism by reducing activation energy between reactants and products

4 Consider the following plot between $\ln k$ and $1/T$,



In this plot, the intercept and slope respectively are

(a) $-\frac{E_a}{R}$; $\ln A$ (b) $\ln A$; $-\frac{E_a}{R}$
(c) $\frac{E_a}{R}$; $-\ln A$ (d) $\frac{E_a}{R}$; A

CASE BASED Questions

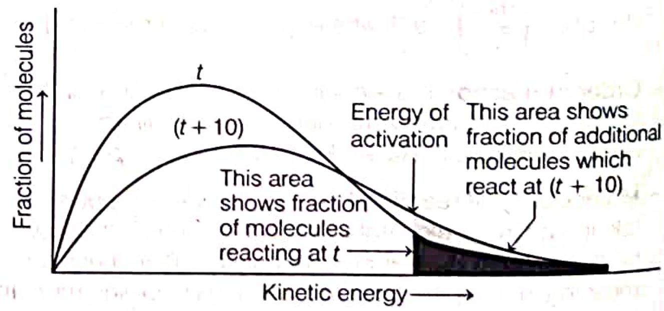
Case I

Most of the chemical reactions are accelerated by increase in temperature T. At a particular temperature T, all the molecules of reactants do not have the same kinetic energy but the fractions of molecules having particular kinetic energies at a particular temperature remain constant. The distribution of kinetic energy may be described by plotting the fraction of molecules (N_E/N_T) with a given kinetic energy (E). This is called Maxwell's Boltzmann distribution of energies. Here, N_E is the number of molecules with energy E and N_T is the total number of molecules.

The temperature dependence of rate of a chemical reaction is expressed by Arrhenius equation, $k = Ae^{-E_a/RT}$

The following questions are multiple choice questions. Choose the most appropriate answer :

5 Given the Maxwell's Boltzmann's distribution curve showing dependence of rate of reaction.



(a) time (b) conc. of reactant
(c) amount of reacant (d) temperature

6 What does the peak of the distribution curve represents?

(a) Kinetic energy (b) Potential energy
(c) Number of molecules (d) Time

7 What does the graph show that on increasing the temperature rate of reaction gets doubled?

(a) Doubles the concentration of reactants
(b) half the amount of reactant
(c) double the rate of reaction
(d) half the rate of reaction

Or The rate constant of a reaction is $1.5 \times 10^7\ s^{-1}$ at 50°C and $4.5 \times 10^{-7} s^{-1}$ at 100°C. Calculate the value of activation energy E_a for the reaction $R = 8.314\ J\ K^{-1}\ mol^{-1}$.

(a) 22.01 J mol^{-1} (b) 22.01 kJ mol^{-1}
(c) 19.15 J mol^{-1} (d) 19.5 kJ mol^{-1}

8 With the help of Arrhenius equation, what will be the effect on increasing the temperature result in .... in the rate of reaction?

(a) increase (b) decrease
(c) constant (d) None of these

Case II

Read the passage given below and answer the questions that follows

Are there nuclear reactions going on in our bodies?

There are nuclear reactions constantly occurring in our bodies, but there are very few of them compared to the chemical reactions, and they do not affect our bodies much. All of the physical processes that take place to keep a human body running are chemical processes. Nuclear reactions can lead to chemical damage, which the body may notice and try to fix.

The nuclear reaction occurring in our bodies is radioactive decay. This is the change of a less stable nucleus to a more stable nucleus. Every atom has either a stable nucleus or an unstable nucleus, depending on how big it is and on the ratio of protons to neutrons. The ratio of neutrons to protons in a stable nucleus is thus around 1:1 for small nuclei ($Z <$ 20). Nuclei with too many neutrons, too few neutrons, or that are simply too big are unstable. They eventually transform to a stable form through radioactive decay. Wherever there are atoms with unstable nuclei (radioactive atoms), there are nuclear reactions occurring naturally.

The most common natural radioactive isotopes in humans are carbon-14 and potassium-40. Chemically, these isotopes behave exactly like stable carbon and potassium. For this reason, the body uses carbon-14 and potassium-40 just like it does normal carbon and potassium; building them into the different parts of the cells, without knowing that they are radioactive. In time, carbon-14 atoms decay to stable nitrogen atoms and potassium-40 atoms decay to stable calcium atoms. Chemicals in the body that relied on having a carbon-14 atom or potassium-40 atom in a certain spot will suddenly have a nitrogen or calcium atom. Such a change damages the chemical. Normally, such changes are so rare, that the body can repair the damage or filter away the damaged chemicals.

The natural occurrence of carbon-14 decay in the body is the core principle behind carbon dating. As long as a person is alive and still eating, every carbon-14 atom that decays into a nitrogen atom is replaced on average with a new carbon-14 atom. But once a person dies, he stops replacing the decaying carbon-14 atoms. Slowly the carbon-14 atoms decay to nitrogen without being replaced, so that there is less and less carbon-14 in a dead body.

The rate at which carbon-14 decays is constant and follows first order kinetics. It has a half - life of nearly 6000 years, so by measuring the relative amount of carbon-14 in a bone, archeologists can calculate when the person died. All living organisms consume carbon, so carbon dating can be used to date any living organism, and any object made from a living organism. Bones, wood, leather, and even paper can be accurately dated, as long as they first existed within the last 60,000 years. This is all because of the fact that nuclear reactions naturally occur in living organisms.

CBSE SQP (Term II)

9. Why is carbon -14 radioactive while carbon -12 not? (Atomic number of carbon = 6)

10. Researchers have uncovered the youngest known dinosaur bone, dating around 65 million years ago. How was the age of this fossil estimated?

11. Which are the two most common radioactive decays happening in human body?

12. Suppose an organism has 20 g of carbon -14 at its time of death. Approximately how much carbon -14 remains after 10,320 years? (Given antilog 0.517 = 3.289)

Or

Approximately how old is a fossil with 12 g of carbon -14, if it initially possessed 32 g of carbon -14? (Given log 2.667 = 0.4260)

Case III

(Read the passage given below and answer the following questions)

The rate of a reaction, which may also be called its velocity or speed, can be defined with relation to the concentration of any of the reacting substances, or to that of any product of the reaction. If the species chosen is a reactant which has a concentration c at time t the rate is $- dc/dt$, while the rate with reference to a product having a concentration x at time

t is dx/dt. Any concentration units may be used for expressing the rate; thus, if moles per liter are employed for concentration and seconds for the time, the units for the rate are moles liter $^{-1}$sec^{-1}. For gas reactions pressure units are sometimes used in place of concentrations, so that legitimate units for the rate would be (mm Hg) sec^{-1} and atm sec^{-1}.

The order of a reaction concerns the dependence of the rate upon the concentrations of reacting substances; thus, if the rate is found experimentally to be proportional to the α^{th} power of the concentration of one of the reactants A, to the β^{th} power of the concentration of a second reactant B, and so forth, *via.*,

$$\text{rate} = kC_A{}^{\alpha}C_B^{\beta} \qquad \ldots\text{(i)}$$

the overall order of the reaction is simply

$$n = \alpha + \beta + \ldots \qquad \ldots\text{(ii)}$$

Such a reaction is said to be of the α^{th} order with respect to the substance A, the β^{th} order with respect to B and so on...

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

CBSE Question Bank

13 **Assertion** Rate of reaction is a measure of change in concentration of reactant with respect to time.
Reason Rate of reaction is a measure of change in concentration of product with respect to time.

14 **Assertion** For a reaction: $P + 2Q \longrightarrow$ products, Rate $= k[P]^{1/2}[Q]^1$ so the order of reaction is 1.5
Reason Order of reaction is the sum of stoichiometric coefficients of the reactants.

15. **Assertion** The unit of k is independent of order of reaction.
Reason The unit of k is moles $L^{-1}s^{-1}$.

16 **Assertion** Reactions can occur at different speeds.
Reason Rate of reaction is also called speed of reaction.

ASSERTION and REASON

■ **Directions** (Q. Nos. 17-24) *In the following questions, an Assertion (A) is followed by a corresponding Reason (R) Use the following keys to choose the appropriate answer.*

(a) Both (A) and (R) are correct, (R) is the correct explanation of (A).
(b) Both (A) and (R) are correct, (R) is not the correct explanation of (A).
(c) (A) is correct; (R) is incorrect.
(d) (A) is incorrect; (R) is correct.

17 **Assertion** (A) $\Delta[R]$ is multiplied with -1 to make the rate of the reaction a positive quantity.
Reason (R) $\Delta[R]$ is a negative quantity in the expression, rate of disappearance of $R = \dfrac{-\Delta[R]}{\Delta t}$

18 **Assertion** (A) Some zero order reactions may have order in fractions.
Reason (R) Order cannot be determined from balanced chemical equation.

19 **Assertion** (A) Decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.
Reason (R) At high pressure, the metal surface gets saturated with gas molecules.

20 **Assertion** (A) A catalyst increases the rate of reaction.
Reason (R) Catalyst also changes the equilibrium constant.

21 **Assertion** (A) A positive catalyst increases the rate of reaction.
Reason (R) A catalyst increases the rate of reaction by making available a new and more efficient mechanism.

22 **Assertion** (A) Order of reaction can be zero or fractional.
Reason (R) We cannot determine order from balanced chemical equation.

23 **Assertion** (A) All collisions of reactant molecules lead to product formation.
Reason (R) Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

24 **Assertion** (A) Rate constant determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.
Reason (R) Reactant molecules undergo chemical change irrespective of their orientation during collision.

VERY SHORT ANSWER Type Questions

25 Which type of reactions are usually very fast?

26 When does the rate of reaction is equal to specific reaction rate?

27 How does the value of rate constant vary with reactant concentration?

28 Under what conditions, a bimolecular reaction is kinetically first order?

29 For a reaction, $X + H_2O \longrightarrow Y$, rate $\propto [X]$.

What is its

(i) molecularity? (ii) order of reaction?

30 In what case order of reaction is equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction?

31 Why does the hydrolysis of ethyl acetate being a bimolecular reaction is said to be a first order reaction?

32 What is the value of rate constant at an extremely high temperature? Is this rate constant feasible?

33 If the reaction has the rate constant 1.9×10^{-4} atm^{-1}s^{-1} then predict the order of the reaction.

34 If the rate of any reaction is Rate $= k[A]^1[B]^1$ then, what is the order of the reaction?

35 A substance disintegrated 87.5% in 45 min. What is its half-life?

SHORT ANSWER Type I Questions

36 The rate of a reaction is given by rate $= k[N_2O_5]$.

In this equation, what does k stand for? What is meant by elementary step in a reaction?

37 One-fourth of reaction is completed in 32 min. What is the half-life period of this reaction? How is half-life period related to initial concentration for a second order reaction?

38 Find the molecularity of the reaction, $Cl \longrightarrow \frac{1}{2} Cl_2(g)$. Give the potential energy diagram to explain activation energy.

39 (i) Illustrate graphically the effect of catalyst on activation energy.

(ii) Catalysts have no effect on the equilibrium constant, why?

40 State the role of activated complex in a reaction and state its relation with activation energy.

41 $A + 2B \longrightarrow 3C + 2D$

The rate of disappearance of B is 0.5×10^{-3} mol L^{-1} s^{-1}. What will be

(i) rate of the reaction?

(ii) rate of change in concentration of A and C?

42 The concentration of R in the reaction; $R \longrightarrow P$; was -measured as a function of time and the following data is obtained:

$[R]$ mol L^{-1}	1.0	0.75	0.40	0.10
t (min)	0.0	0.05	0.12	0.18

Determine the order of reaction.

43 For a reaction $P \rightarrow Q$, the rate becomes 27 times when concentration of P is tripled. What is the order of the reaction?

44 The rate constant of a reaction of zero order in A is 3.0×10^{-3} mol L^{-1} s^{-1}. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M?

45 For a reaction, $X(g) \longrightarrow Y(g) + Z(g)$ the half-life period is 10 min. In what period of time would the concentration of X be reduced to 10% of original concentration?

46 The half-life period of a first order reaction is 60 min. What percentage will be left after 120 minutes?

47 If time taken for half of the first order reaction to complete is t_1, whereas that for $3/4^{th}$ of the reaction to complete is t_2. How are t_1 and t_2 related to each other?

48 The rate of a chemical reaction doubles for every 10°C rise in temperature. If the temperature is raised from 10° to 30°C, what will be the increase in the rate of the reaction?

49 The activation energy of a reaction is 94.14 kJ mol^{-1} and the value of rate constant at 298 K is 18×10^{-5}s^{-1}. Calculate the frequency factor or pre-exponential factor, A.

50 If the rate constants of a reaction are 1×10^3 s^{-1} and 2×10^3 s^{-1} at 27°C and 37°C, respectively. Calculate the activation energy (E_a) of the reaction.

51 In the Arrhenius equation for a certain reaction, the value of A (frequency factor) and E_a (activation energy) are $4 \times 10^{13}\ s^{-1}$ and $98.6\ kJ\ mol^{-1}$, respectively. If the reaction is of first order, then find that at what temperature will its half-life period be 10 min?

52 When the temperature of a reaction is raised from 47°C to 57°C, the rate of the chemical reactions is doubled. Calculate the E_a. (Given, $R = 8.314\ J\ mol^{-1}\ K^{-1}$)

53 For a reaction, the energy of activation is zero. What is the value of rate constant at 300 K, if $k = 1.6 \times 10^6 s^{-1}$ at 280 K?

54 Derive the equation for the rate constant of a first order reaction and show that the time required for the completion of half of the first order reaction is independent of initial concentration.

55 What will be the initial rate of a reaction if its rate constant is $10^{-3}\ min^{-1}$ and the concentration of reactant is $0.2\ mol\ dm^{-3}$? How much of the reactant will be converted into products in 200 min?

56 The rate constant for a first order reaction is $60\ s^{-1}$. How much time will it take to reduce the concentration of the reactant of 1/10 th of its initial value?

57 The decomposition of N_2O_5 according to the equation.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

is a first order reaction. After 30 min, in a closed vessel, the total pressure is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Then, find the rate constant of the reaction.

SHORT ANSWER Type II Questions

58 Half-life of a first order reaction is $8 \times 10^4 s$. What percentage of the initial reactant will react in 2 h?

59 The rate of first order reaction is $0.04\ mol\ L^{-1}s^{-1}$ at 10 min and $0.03\ mol\ L^{-1}s^{-1}$ at 20 min after initiation. Thus, find the half-life of the reaction.

60 The rate constant of a certain reaction is given by

$$\log k = 6.8 - \frac{213}{T} + 5.7 \log T$$

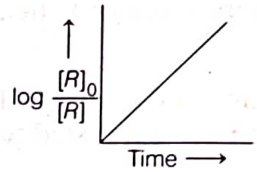
Calculate E_a at 127°C.

61 The activation energy of a first order reaction is $187.06\ kJ\ mol^{-1}$ at 750 K and the value of pre-exponential factor, A is $1.97 \times 10^{12}\ s^{-1}$. Calculate the rate constant and half-life. (Given : $e^{-30} = 9.35 \times 10^{-14}$)

62 The rate of a particular reaction triples when temperature changes from 60°C to 100°C. Calculate the activation energy of the reaction.

LONG ANSWER Type Questions

63 Consider the reaction, $A \xrightarrow{k} B$. The change in concentration with time t is shown in the graph.



(i) Predict the order of the reaction.

(ii) Derive the expression for the time which is required to complete the reaction.

(iii) Find the slope of the curve.

64 A drug becomes ineffective after 30% decomposition. The original concentration was $10\ mg\ mL^{-1}$ which becomes $8.4\ mg\ mL^{-1}$ during first 40 months. Assuming the decomposition of first order, calculate the expiry time of the drug in months. What is the half-life of the drug?

65 The experimental data for the reaction;

$$2A + B_2 \longrightarrow 2AB;\ \text{is}$$

Experiment	$[A]$ M	$[B_2]$ M	Initial rate (mol $L^{-1}\ s^{-1}$)
1.	0.50	0.5	1.6×10^{-4}
2.	0.50	1.0	3.2×10^{-4}
3.	1.00	1.0	3.2×10^{-4}

Write the most probable rate equation for the reaction.

66 $^{238}_{92}U$ changes to $^{206}_{92}Pb$ by successive radioactive decay. A sample of uranium was analysed and found to contain 1.0 g of ^{238}U and 0.1 g of ^{206}Pb had accumulated due to decay of ^{238}U, find out the age of ore. (Half-life of $^{238}U = 4.5 \times 10^9$ years)

ANSWERS

1 (a) **2** (b) **3** (b) **4** (b)

5 (*d*) This curve is showing temperature dependence of rate of reaction.

6 (*a*) The peak of the curve represents the kinetic energy possessed by the maximum fraction of molecules that is known as most probable kinetic energy.

7 (*c*) The graph shows that in the curve at $(t+10)$ the area showing the fraction of reacting molecules having energy equal to or greater than activation energy gets doubled and hence, doubles the rate of a reaction.

Or (*d*) From Arrhenius equation, we have

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{4.5 \times 10^7 \text{s}^{-1}}{1.5 \times 10^7 \text{ s}^{-1}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{323} - \frac{1}{373}\right]$$

$$E_a = \frac{0.4771 \times 19.147 \times 323 \times 373}{50}$$

$$E_a = 22011.59 \text{ J mol}^{-1} \text{ or } 22.01 \text{ kJ mol}^{-1}$$

8 (*a*) In Arrhenius equation, $k = Ae^{-E_a/RT}$, the factor $e^{-E_a/RT}$ represents the fraction of molecules that have kinetic energy more than the activation energy (E_a). Thus, it is clear from Arrhenius equation that increasing the temperature or decreasing the activation energy will result in an increase in the rate of reaction.

9 C-14 and C-12 have same number of protons (i.e. 6) but different number of neutrons (i.e. 8 and 6 respectively).

As C-14 atom has more neutrons than protons in its nucleus, therefore, its nucleus becomes unstable and shows radioactivity.

10 Radioactive or carbon dating method is used to find out the age of fossils.

11 The two most common radioactive decays happening in human body are

(a) carbon-14 decay to stable nitrogen atom and

(b) potassium-40 atoms decay to stable calcium.

12 Given, amount of C -14(C_0) = 20 g

Time = 10,320 years

According to first order, $t_{1/2} = \dfrac{0.693}{k}$

$$k = \frac{0.693}{6000}$$

[$t_{1/2} = 6000$ given in the passage]

For 1st order reactions

$$t = \frac{2.303}{k}\log\left[\frac{C_0}{C_t}\right]$$

On putting the value in first order equation, we get

$$10,320 = \frac{2.303}{0.693} \times 6000 \log\left[\frac{20}{C_t}\right]$$

[Let C_t be the amount of C-14 remains after 10,320 years]

$$\log\left(\frac{20}{C_t}\right) = \frac{10,320 \times 0.693}{2.303 \times 6000} = 0.517$$

$$\frac{20}{C_t} = \text{antilog } (0.517)$$

$$C_t = \frac{20}{3.2089} = 6.197\text{g}$$

Or

Given, initial amount of C-14 present in fossil $C_0 = 32$ g

Final amount of C-14, i.e. $C_t = 12$g.

Time $(t) = ?$

For 1st order reaction, $k = \dfrac{0.693}{6000}$

[half-life, i.e. 6000, is given in passage]

For 1st order reactions

$$t = \frac{2.303}{k}\log\left(\frac{C_0}{C_t}\right) \quad \text{...(i)}$$

Substituting the given value in Eq. (i),

we get

$$t = \frac{2.303}{0.693} \times 6000 \times \log\frac{32}{12}$$

$$= 19939.4 \log 2.667$$

$$= 19939.4 \times 0.426$$

$$= 8494 \text{ years}$$

13 (*b*) Rate of reaction is measure of change in concentration of reactant and product with respect to time. As, concentration of product increases with increase in time, concentration of reactant decreases.

For reaction $R \rightarrow P$

$$\text{Rate} = \frac{-\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$$

14 (*c*) Order of reaction depends on the concentration of reacting substances. Thus, if the rate is found experimentally proportional to the α^{th} power of concentration of one of the reactants *A*, to the β^{th} power of the concentration of a second reactant *B*. Then,

$$\text{Rate} = kC_A^{\alpha}C_B^{\beta}$$

Overall order of the reaction is simply, $n = \alpha + \beta$

15 (*d*) The unit of *k* depends on order of reaction and it is moles $\text{L}^{-1}\text{ S}^{-1}$.

16 (*b*) Rate of reaction can be different for every reaction. Rate of reaction is also known as speed of reaction or velocity of reaction. It is defined as the change in concentration of reactant or product in unit time.

17 (a) Rate of disappearance of $R = -\frac{\Delta[R]}{\Delta t}$

Since, $\Delta[R]$ is a negative quantity, it is multiplied with -1 to make the reaction rate a positive quantity. Hence, both (A) and (R) are correct and (R) is the correct explanation of (A).

18 (d) Only reactions with zero order do not have the order in fractions. Thus, (A) is incorrect but (R) is correct.

19 (a) It is a zero order reaction at high pressure.

$$2NH_3(g) \xrightarrow[\text{Pt catalyst}]{1130\text{ K}} N_2(g) + 3H_2(g)$$

Rate $= k\,[NH_3]^0 = k$

In this reaction, Pt acts as a catalyst the metal surface gets saturated with gas molecules at high pressure. Thus, a further change in reaction conditions does not alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration. Thus, both (A) and (R) are correct and (R) is the correct explanation of (A).

20 (c) A small amount of the catalyst can catalyse a large amount of reactants. A catalyst does not alter Gibbs energy, ΔG of a reaction. It does not change the equilibrium constant rather, it helps in attaining the equilibrium faster, i.e. it catalyses the forward and backward directions both to the same extent so that the equilibrium state remains same and is achieved earlier. Thus, (A) is correct but (R) is incorrect.

21 (a) A positive catalyst increases rate of reaction by making a new and more efficient mechanism. Thus, both (A) and (R) are correct and (R) is the correct explanation of (A)

22 (b) Order of reaction can be zero or fractional as order of reaction is directly related to sum of power of reactants. Hence, both (A) and (R) are correct and (R) is the correct explanation of (A).

23 (c) Only effective collision lead to formation of product in a chemical reaction. Thus, (A) is correct but (R) is incorrect.

24 (c) (A) is correct but (R) is incorrect. The correct explanation is reactant molecules which have proper orientation during collision and sufficient kinetic energy lead to the chemical change.

25 Refer to text on pages 92.

26 When concentration of all the reactants is unity, then Rate = k

27 Rate constant value does not depend upon the concentrations of the reactions.

28 When one of the reactant is present in large amount.

29 (i) molecularity = 2 (ii) order = 1

30 In elementary reactions, molecularity is equal to the order of the reaction.

31 $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

Rate $= k\,[CH_3COOC_2H_5]\,[H_2O]^0$

32 $k = Ae^{-E_a/RT}$

$k = A$, if $T \to \infty$

33 Second order reaction.

34 [Ans 2nd order reaction]

35 Calculate k followed by $t_{1/2}$.

Rate constant, $k = \frac{2.303}{t}\log\frac{a}{a-x}$

Half time $(t_{1/2}) = \frac{0.693}{k}$ [Ans $t_{1/2} = 26$ min]

36 Refer to text on page 93. k stands for rate constant.

37 $t_{1/2} = \frac{0.0693}{k}$

Half life, $t_{1/2} \propto \frac{1}{[R]_0^{n-1}}$

38 Refer to text on page 102 and 120.

39 Refer to text on page 120 and 121.

40 Refer to text on page 118 and 119.

41 Rate $= -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = +\frac{1}{3}\frac{d[C]}{dt} = -\frac{1}{2}\frac{d[D]}{dt}$

42 Rate law states that, Rate $= k[A]^x[B]^y$

Refer to solution 14 on page 114.

[Ans First order reaction]

43 Third order reaction.

44 $t = \frac{1}{k}\{[A]_0 - [A]\}$ [Ans $t = 8.35$ s]

45 $t_{1/2} = \frac{0.693}{k}$, $t = \frac{2.303}{k}\log\frac{a}{a-x}$ [Ans 33 min]

46 $k = \frac{0.693}{t_{1/2}}$, $t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$ [Ans 25%]

47 $t_{3/4} : t_{1/2} = 2$

48 3 times.

49 According to Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303RT}$$

We have, $k = 18\times10^{-5}\text{s}^{-1}$,

$E_a = 94.14$ kJ mol^{-1},

$T = 298$ K, $R = 8.314$ JK^{-1} mol^{-1}

$$\log A = \log K + \frac{Ea}{2.303RT}$$

$$= \log(18\times10^{-5}\text{s}^{-1}) + \frac{94140\text{ J mol}^{-1}}{2.303\times(8.314\text{ J K}^{-1}\text{ mol}^{-1})\times 298\text{ K}}$$

$\log A = -3.744 + 16.5 = 12.756$

$A = \text{antilog}(12.756) = 5.7\times10^{12}\text{s}^{-1}$

50 **Hint** Given, $k_1 = 1\times10^3\text{s}^{-1}$, $k_2 = 2\times10^3\text{s}^{-1}$

$T_1 = 300$ K. $T_2 = 310$ K, $R = 8.314$ JK^{-1}mol^{-1}

$$\log\frac{k_2}{k_1} = -\frac{E_a}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

51 $A = 4 \times 10^{13} s^{-1}$, $E_a = 98.6$ kJ mol^{-1}

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\log k = \log(4 \times 10^{13}) - \frac{98600}{2.303 \times 8.314 \times T}$$

Now, $t_{1/2} = \frac{0.693}{k}$ [For first order reaction]

$$k = \frac{0.693}{600 s} = 1.155 \times 10^{-3} s^{-1}$$

$$\log(1.155 \times 10^{-3}) = \log(4 \times 10^{13}) - \frac{98600}{2.303 \times 8.314 \times T}$$

$$2.93 = \frac{13.60 - 5149.6}{T} \Rightarrow T = 311.53 \text{ K}$$

52 Hint Use Arrhenius equation, $\log k = \log A - \frac{E_a}{2.303RT}$

53 Hint $\log \frac{k_2}{k_1} = -\frac{E_a}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$

$\therefore k_2 = k_1$

54 Refer to text on pages 108 and 110.

55 Use, $k = \frac{2.303}{t} \log \frac{a}{a-x}$

$$10^{-3} = \frac{2.303}{12 \times 10^3 s} \log \frac{0.2}{a-x}; \quad \log \frac{0.2}{a-x} = 5.210$$

$$0.2 = 1.62181 (a-x) \Rightarrow a - x = 1.23 \times 10^{-5}$$

56 $k = \frac{0.693}{t_{1/2}}$ and then use the equation

$$t = \frac{2.303}{k} \log \frac{a}{a-x} \quad [\text{Ans. } t = 3.8 \times 10^{-2} s]$$

57 Use, $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$

Refer to Example 2 on page 109.

58 $t_{1/2} = 8 \times 10^4 s$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{8 \times 10^4} = 8.66 \times 10^{-6}$$

Then, use $k = \frac{2.303}{t} \log \frac{a}{a-x}$

59 $k = \frac{2.303}{t} \log \frac{a}{a-x}$

$$k = \frac{2.303}{600 \text{ s}} \log \frac{0.04}{0.03} \Rightarrow k = 4.8 \times 10^{-4}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.8 \times 10^{-4}} = 1.44 \times 10^3 s$$

60 Compare the given equation by

$$\log k = \log A - \frac{E_a}{2.303RT}$$

And then calculate E_a.

61 $\log k = \log A - \frac{E_a}{2.303RT}$

$$\log k = \log(1.97 \times 10^{12}) - \frac{187060}{2.303 \times 8.314 \times 750}$$

$$\log k = 12.3 - 13.026 \Rightarrow \log k = -0.726$$

$$k = 0.188$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.188} = 3.686$$

62 Refer to solution 19 on page 124.

63 Refer to text on page 108.

64 Use, $k = \frac{2.303}{t} \log \frac{a}{a-x}$

65 Refer to Example 4 on page 97.

66 Refer to Example 3 on page 110.
[Ans 7.099×10^8 years]

04

d-AND *f*-BLOCK ELEMENTS

The *d*-block of the periodic table includes the elements of the groups 3 to12, in which the *d*-orbitals are progressively filled in each of the four long periods. The elements constituting the *f*-block are those in which the 4*f*-and 5*f*-orbitals are progressively filled in the latter two long periods. These elements are formal members of group 3 from which they have been taken out to develop a separate *f*-block of the periodic table. Generally, the terms '**transition metals**' and '**inner-transition metals**' are used to refer the elements of *d*-and *f*-blocks, respectively.

The two series of the inner-transition metals (4*f* and 5*f*) are written separately, outside the periodic table and are called **lanthanoids** and **actinoids**, respectively.

CHAPTER CHECKLIST

- Transition Elements and Their Properties
- Important Compounds and Applications of Transition Elements
- Inner-Transition Elements

|TOPIC 1|
Transition Elements and Their Properties

d-BLOCK ELEMENTS

The elements which have incompletely filled *d*-orbitals in its ground state or in any of its oxidation state are called *d*-**block elements** (transition elements).

As zinc (Zn), cadmium (Cd), mercury (Hg) of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states, thus they are not regarded as transition metals, but they are studied along with the chemistry of the transition metals.

The presence of partly filled *d*-or *f*-orbitals in their atoms sets the study of the transition elements and their compounds apart from that of the main group elements. Still, the usual theory of valence as applicable to the main group elements can also be applied successfully to the transition elements.

Various precious metals like silver, gold and platinum, and industrially important metals like iron, copper and titanium form part of the transition metals.

Position of d-Block Elements in the Periodic Table

The *d*-block occupies the large middle section flanked between *s*-and *p*-blocks in the periodic table. The name 'transition' given to the elements of *d*-block is only because of their position between *s*-and *p*-block elements. The *d*-orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals, i.e. $3d$, $4d$ and $5d$. The fourth row of $6d$ is still incomplete.

First transition series or $3d$- series Scandium ($_{21}Sc$) to Zinc ($_{30}Zn$).

Second transition series or $4d$-series Yttrium ($_{39}Y$) to Cadmium ($_{48}Cd$).

Third transition series or $5d$-series Lanthanum ($_{57}La$) to Mercury ($_{80}Hg$). Excluding $_{58}Ce$ to $_{71}Lu$.

Fourth transition series or $6d$-series Actinium ($_{89}Ac$) to Copernicium ($_{112}Cn$) excluding $_{90}Th$ to $_{103}Lr$.

Electronic Configuration of the d-Block Elements

General electronic configuration of transition metals is $(n-1)\,d^{1\text{-}10}\,ns^{1\text{-}2}$, where n is the outermost shell which may have one or two electrons, whereas $(n-1)$ stands for the inner *d*-orbitals which may have one to ten electrons.

Exception

(i) All the *d*-block elements however, are not transition elements. Last members of different series such as Zn, Cd and Hg has completely filled *d*-orbital $(n-1)\,d^{10}\,ns^2$. The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. These do not show any characteristic properties of transition elements except complex formation. Hence, these elements are not considered as transition elements.

(ii) Some of the exceptions are observed in electronic configuration due to very little energy difference between $(n-1)d$ and ns orbitals such as

$$Cr : 3d^5, 4s^1 \text{ instead of } 3d^4, 4s^2$$

$$Cu : 3d^{10}, 4s^1 \text{ instead of } 3d^9, 4s^2$$

This can be explained on the basis of electronic repulsion and energy exchange which proves that half-filled and completely filled *d*-orbital are more stable configuration.

In the transition elements, the *d*-orbitals project to the periphery of an atom more than the other orbitals (i.e. *s* and *p*). Thus, they are more influenced by the surroundings as well as affecting the atoms or molecules surrounding them.

In some respect, ions of a given d^n configuration (n = 1- 9) have similar electronic and magnetic properties. With partly half-filled *d*-orbitals, these elements exhibit certain characteristic properties like display of various oxidation states, coloured ions formation and entering into complex formation with a variety of ligands. These elements also possess catalytic property and paramagnetic behaviour.

Outer electronic configuration of transition elements (Ground State)

1st series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

2nd series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	5	7	8	10	10	10

3rd series

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

4th series

	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Z	89	104	105	106	107	108	109	110	111	112
7s	2	2	2	2	2	2	2	2	1	2
6d	1	2	3	4	5	6	7	8	10	10

Lattice structures of transition metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
hcp (bcc)	hcp (bcc)	bcc	bcc (bcc, ccp)	X (hcp)	bcc (hcp)	ccp	ccp	ccp	X (hcp)
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
hcp (bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X (hcp)
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
hcp (ccp, bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X

(bcc = body centred cubic, hcp = hexagonal close packed, ccp = cubic close packed, X = a typical metal structure)

General Properties of the Transition Elements (*d*-Block)

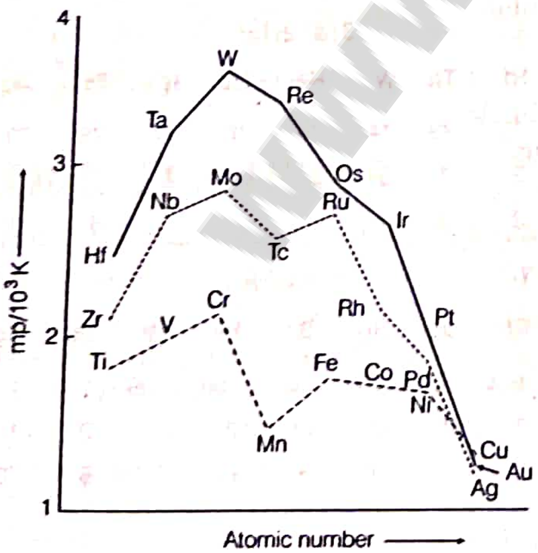
Physical Properties

(i) Transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre. With the exceptions of Zn, Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.

(ii) They are very much hard and have very low volatility except Zn, Cd and Hg.

(iii) They have high melting and boiling points. The high melting point of these metals is due to the involvement of greater number of electrons from $(n-1)d$ in addition to the *ns*-electrons in the interatomic metallic bonding.

(iv) In any row, the melting points of these metals rise to a maximum at d^5 and fall regularly with the increase in atomic number except Mn and Tc.



Trends in melting points of transition elements

(v) They have high enthalpies of atomisation.

Enthalpy of Atomisation

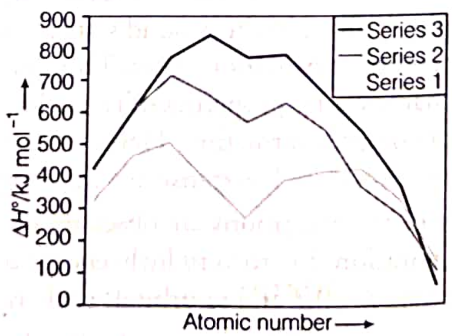
Energy required to convert metallic crystal into individual atom is known as enthalpy of atomisation. The transition metals have high enthalpy of atomisation. It first increases, reaches to the maximum in the middle of each series and then decreases.

It can be explained on the basis of strong interatomic interaction due to unpaired electrons. Greater the number of unpaired electrons, stronger is the resultant bonding.

Enthalpy of atomisation is an important factor in determining the standard electrode potential of a metal, thus metals with high value of enthalpy of atomisation (i.e. very high boiling point) tend to be noble in their reactions.

TRENDS IN ENTHALPIES OF ATOMISATION OF TRANSITION ELEMENTS

Metals of second (4 *d*) and third (5 *d*) series have high enthalpy of atomisation than the corresponding elements of first (3*d*) series because of stronger metal-metal bond. This is an important factor in accounting for the occurrence of much more frequent metal-metal bonding in compounds of the heavy transition metals.

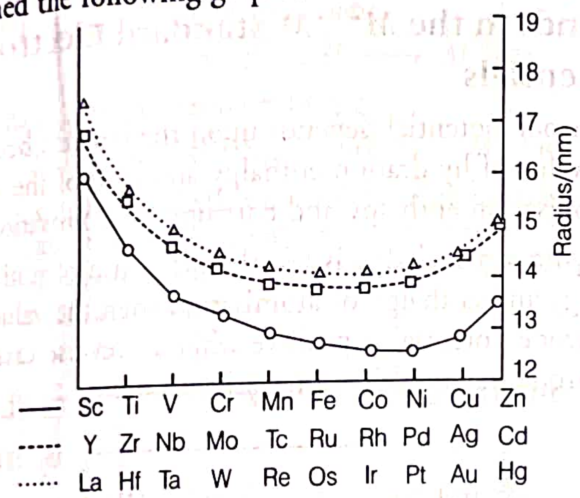


Variation in Atomic and Ionic Sizes of Transition Metals

Atomic/ionic size is expressed in terms of radii. Atomic and ionic radii decrease with increase in atomic number. However, variation within a series is quite small. This is

because the new electron enters a d-orbital each time the nuclear charge increases by unity. Due to poor shielding of d-electrons, attractive forces increase between the nucleus and valence electrons and hence size decreases. However, at the end of the series, size of elements increases due to the increase in the magnitude of repulsive forces between electrons.

On comparing atomic sizes of one series with those of the corresponding elements of the other series, we obtained the following graph :



Trends in atomic radii of transition elements

As it is clear from the above figure that there is an increase in the curve from the first ($3d$) to the second ($4d$) series of the elements but the radii of the third ($5d$) series are virtually the same as those of the corresponding second series members. The reason is the intervention of the $4f$-orbitals which must be filled before the $5d$ series of elements. The filling of $4f$-orbital before $5d$-orbital results in a regular decrease in atomic radii called lanthanoid contraction (discussed later in this chapter).

As a result, density of transition metals increases from left to right in a period because atomic radius decreases and atomic mass increases.

Note Lanthanoid contraction is a special characteristic of lanthanoids as they occupy the same position in periodic table. Due to this contraction, the second and third d series exhibit similar radii, e.g. Zr (160 pm) and Hf (159 pm) have similar physical and chemical properties.

Ionisation Enthalpies (IE)

Ionisation enthalpy is generally high for each series of transition elements due to increase in nuclear charge which accompanies the filling of d-orbitals leading to small size of atoms. For a particular transition series, ionisation enthalpy increases generally on moving from left to right. The relative difference of ionisation enthalpies of any two successive d-block elements of particular period is much smaller than that of s-and p-block elements.

The explanation is that the variation in ionisation enthalpy within the d-block is small due to the screening effect and attractive force acting together. The lower valence state is ionic and the higher valence state is covalent. Ionisation enthalpy increases from left to right in a series, but irregularities are observed due to irregular trends in electronic configuration.

First ionisation energy $(IE)_1$ of $5d$-elements are higher than those of the $3d$ and $4d$-elements. This is due to greater effective nuclear charge acting on outer valence electrons because of the weak shielding of the nucleus by $4f$-electrons. The ionisation energies of the $3d$ and $4d$-elements are irregular.

When the electron is ionised from any transition element, say from iron ($Z = 26$) of $3d$-series, the effective nuclear charge experienced by the $3d$-electrons is greatly enhanced over that of any $4s$-electron. Thus, ionisation of two or more electrons from an atom of a transition element will take place with the removal of s-electrons in preference to the d-electron.

In $3d$-series, first four members show little difference in values and last four are also fairly close. Zn shows quite high value due to extra stability of completely filled orbitals. There is a fall in IE_2 from Cr to Mn and from Cu to Zn because after the removal of first electron, Cr and Cu acquire a stable configuration, i.e. d^5 and d^{10}. The high values of IE_3 for Cu, Ni and Zn explain why they show a maximum oxidation state of +2.

Oxidation States

Transition metals show a great variety of oxidation states in its compounds (variable valency) except the first and the last element. This is because of the fact that the difference in the energy of $(n-1)$ d-electrons and ns-electrons is low which implies that electrons from both energy levels can take part in bonding.

Oxidation states of the first row transition metals
(The most common ones are typed in bold)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	+2
+3	+3	+3	+3	+3	+3	+3	+3	+2	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

For 3d-series In 3d-series, all elements show +2 oxidation state except Sc (Sc = +3). Oxidation states first increases from Sc to Mn due to increase in number of unpaired electrons and then decreases because pairing takes place. Fe and Ni show zero oxidation state in metal carbonyls.

EXAMPLE |1| What may be the stable oxidation state of the transition element with the following d-electron configuration in the ground state of their atoms : $3d^3, 3d^5, 3d^8$ and $3d^4$? **NCERT**

> (i) In case of d-block elements upto 7 group, the maximum oxidation state = ns electrons + $(n-1)d$ unpaired electrons.
> (ii) Minimum oxidation state is generally +2, but in scandium, it is +3.
> (iii) Write the outer shell configuration of the atoms having the given configuration to find the stable oxidation states.

Sol. Stable oxidation states :

$3d^3$: Vanadium (General electronic configuration $3d^3 4s^2$) : oxidation states +2, +3, +4 and +5.

$3d^5$: Chromium (General electronic configuration $3d^5 4s^1$) : oxidation states +3, +4 and +6.

$3d^5$: Manganese (General electronic configuration $3d^5 4s^2$) : oxidation states +2, +4, +6, +7.

$3d^8$: Nickel (General electronic configuration $3d^8 4s^2$) : oxidation states +2, +4.

$3d^4$: Such configuration does not exist in ground state.

Highest Number of Oxidation States

The elements which give the greatest number of oxidation states occur in or near the middle of the series.
e.g. Mn has oxidation states from +2 to +7.

Stability of higher oxidation states increases in a group from top to bottom due to increase in the distance from the outermost shell, e.g. in group 6, Mo (VI) and W (VI) are found to be more stable than Cr (VI). That's why, Cr (VI) in the form of dichromate is a strong oxidising agent, whereas MoO_3 and WO_3 are not.

Variability of oxidation states of transition elements arises due to incomplete filling of d-orbitals in such a way that their oxidation states differ from each other by unity, e.g. $V^{II}, V^{III}, V^{IV}, V^{V}$. On contrary, the variability of oxidation states of non-transition elements, where oxidation states normally differ by a unit of two.

An interesting feature in the variability of oxidation states of d-block elements is noticed among the groups 4 through 10. Although, the lower oxidation states of p-block are favoured by the heavier members due to inert pair effect, the opposite is true in case of d-block elements.

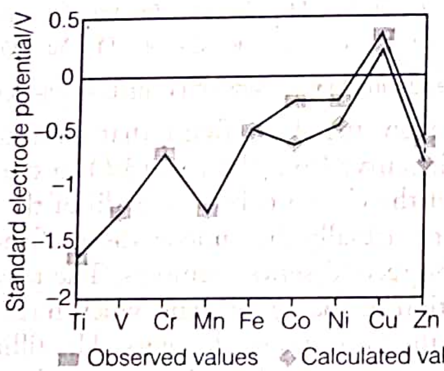
The oxidation state of a metal in a solvent depends on the nature of the solvent, e.g. Cu^+ is unstable in aqueous solution and undergo disproportionation reaction.

Low oxidation states are found if a complex compound has ligands capable of π-acceptor character and σ-bonding, e.g. $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero in the presence of CO as ligand.

Trends in the M^{2+}/M Standard Electrode Potentials

Electrode potential depends upon the balance between the value of hy dration enthalpy and sum of the values of ionisation enthalpy and enthalpy of atomisation.

If hydration enthalpy is less than the sum of ionisation energy and enthalpy of atomisation then the value of electrode potential is positive while in reverse case the electrode potential has a negative value.



Observed and calculated values for the standard electrode potentials ($M^{2+} \rightarrow M^0$) of the elements from Ti to

The explanations are:

(i) The values of E° across the series are less negative because of general increase in the sum of the first and second ionisation enthalpy. E° for Mn and Zn are more negative because of half-filled and fully filled orbitals.

(ii) E° for Ni is more negative due to the highest negative $\Delta_{hyd} H^\circ$. Copper is the only metal having positive value for E° (the sum of enthalpies of sublimation and ionisation is not balanced by hydration enthalpy). This is the reason that it does not liberate H_2 gas from acids. It reacts only with the oxidising acids (HNO_3 and H_2SO_4) which are reduced.

EXAMPLE |2| The $E^\circ_{(M^{2+}/M)}$ value for copper is positive (+0.34 V). What is the possible reason for this? **NCERT Intext**

> Consider the factors on which E° value depends like ionisation enthalpy, hydration enthalpy and enthalpy of atomisation.

Sol. $E^\circ_{(M^{2+}/M)}$ value for any metal depends on three factors:

(i) $\Delta_a H$ (Enthalpy of atomisation);

$$M(s) + \Delta_a H \longrightarrow M(g)$$

(ii) $\Delta_i H$ (Enthalpy of ionisation);

$$M(g) + \Delta_i H \longrightarrow M^{2+}(g)$$

(iii) $\Delta_{hyd} H$ (Hydration enthalpy);

$$M^{2+}(g) + \Delta_{hyd} H\,(aq) \longrightarrow M^{2+}(aq)$$

Copper has high value of enthalpy of atomisation and low value of enthalpy of hydration. It means that $\Delta_i H$ required is not compensated by the energy released. Therefore, $E^\circ_{(Cu^{2+}/Cu)}$ is positive.

Trends in M^{3+}/M^{2+} Standard Electrode Potentials

The low value of E° for Sc^{3+}/Sc^{2+} reflects the stability of Sc^{3+} which has a noble gas configuration. The highest value of E° for Zn^{3+}/Zn^{2+} is due to the removal of an electron from the stable d^{10} configuration of Zn^{2+}.

The comparatively high value of E° for Mn^{3+}/Mn^{2+} indicates the stability of $Mn^{2+}(d^5)$, whereas comparatively low value for Fe indicates the extra stability of Fe^{3+} (d^5). Similarly, the comparative low value for V^{3+}/V^{2+} indicates the stability of V^{2+} (half-filled t_{2g} level discussed in chapter 9).

Trends in Stability of Higher Oxidation States

Transition metals show their highest oxidation states with fluorine and oxygen because F and O are small in size and the most electronegative elements. $3d$ transition metals form stable halides.

The highest oxidation states are shown in TiX_4, VF_5 and CrF_6. While, +7 oxidation state by Mn is shown in the compound MnO_3F. The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice enthalpy as in the case of CoF_3 or higher bond enthalpy, e.g. VF_5 and CrF_6.

In low oxidation states, fluorine is unstable, e.g. VX_2 (X = Cl, Br or I). However, Cu (II) halides are known including CuF_2 except iodide.

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$$

However, most of the Cu(I) compounds are unstable in aqueous solution and undergo disproportionation.

$$2Cu^+(aq) \longrightarrow Cu^{2+} + Cu(s)$$

The stability of $Cu^{2+}(aq)$ than $Cu^+(aq)$ is due to much more negative $\Delta_{hyd}H^\circ$ of $Cu^{2+}(aq)$ than Cu^+, which compensates more for the IE_2 of Cu.

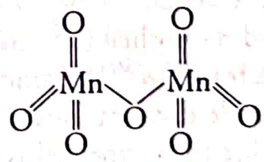
Note Disproportionation is a special type of redox reaction in which a species is simultaneously reduced and oxidised to form two different products. In disproportionation, same substance behaves as oxidising agent for one molecule and at the same time as reducing agent for another molecule.

Formulae of halides of 3*d*-transition metals

Oxidation number	4	5	6	7	8	9	10	11	12
+6			CrF_6						
+5		VF_5	CrF_5						
+4	TiX_4	VX^I_4	CrX_4	MnF_4					
+3	TiX_3	VX_3	CrX_3	MnF_3	FeX^I_3	CoF_3			
+2	TiX^{III}_2	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX^{II}_2	ZnX_2
+1								CuX^{III}	

Key $X = F \rightarrow I$, $X^I = F \rightarrow Br$, $X^{II} = F \rightarrow Cl$, $X^{III} = Cl \rightarrow I$

Oxygen stabilises the highest oxidation state in the oxides more than fluorine (highest fluoride of Mn is MnF_4 whereas highest oxide is Mn_2O_7) due to the ability of oxygen to form multiple bonds with the metal atoms, e.g. in the covalent oxide Mn_2O_7, each Mn is tetrahedrally surrounded by oxygen including a Mn—O—Mn bridge.



Beyond group 7, no higher oxides of Fe above Fe_2O_3 are known, although ferrates (VI) $(FeO_4)^{2-}$ are formed in alkaline medium but they readily decompose to Fe_2O_3 and O_2. Besides the oxides, oxocations stabilise V^V as VO_2^+, V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+}.

Note Highest oxidation state of manganese is +7, exhibited in stable compounds. Although osmium is the element with highest oxidation state in periodic table which is +8.

The tetrahedral $[MO_4]^{n-}$ ions are known for V^V, Cr^{VI}, Mn^V, Mn^{VI} and Mn^{VII}.

Groups containing oxides of 3d-transition metals

Oxidation number	3	4	5	6	7	8	9	10	11	12
+7					Mn_2O_7					
+6				CrO_3						
+5			V_2O_5							
+4		TiO_2	V_2O_4	CrO_2	MnO_2					
+3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3, $Mn_3O_4^*$	Fe_2O_3, $Fe_3O_4^*$	$Co_3O_4^*$			
+2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+1									Cu_2O	

*Mixed oxides

Chemical Reactivity and E° Values

The transition metals show wide variations in their chemical reactivity. Most of them are sufficiently electropositive to dissolve in mineral acids. Some of them are noble and are not affected by single acids.

The metals of first transition series (with the exception of copper) are relatively more reactive and are oxidised by 1 M H^+, however the actual rate of reaction of these metals with oxidising agents like hydrogen ion (H^+) is sometime slow, e.g. Ti and V are passive to dilute non-oxidising acids at room temperature.

The E° values for M^{2+}/M indicate a decreasing tendency to form divalent cations across the series. The general trend towards less negative E° values is related to the increase in the sum of the first and second ionisation enthalpies.

The E° values for Mn, Ni and Zn are more negative than expected from the general trend. It is due to the stabilities of half-filled d-subshell (d^5) in Mn^{2+} and completely filled d-subshell (d^{10}) in zinc. It explains their tendencies to form stable divalent ions. For Ni^{2+}, the more negative E° value than expected is due to its highest negative enthalpy of hydration.

The E° values for M^{3+}/M^{2+} shows that Mn^{3+} and Co^{3+} ions are strong oxidising agents in aqueous solutions due to high positive E° values. Ti^{2+}, V^{2+} and Cr^{2+} ions are strong reducing agents and will therefore liberate H_2 from a dilute acid.

e.g. $2Cr^{2+}(aq) + 2H^+(aq) \longrightarrow 2Cr^{3+}(aq) + H_2(g)$

Magnetic Properties

On applying a magnetic field to substances, two types of magnetic behaviour are observed as **diamagnetism** and **paramagnetism**. The former substances are repelled by applied field whereas the latter ones are slightly attracted. Transition metals have one or more unpaired electron. So, they are paramagnetic in nature.

Paramagnetism arises due to the rotation of electron (spin motion) around the axis and revolution around the nucleus (orbital motion) as the number of unpaired electrons increases, paramagnetism increases.

Those transition elements which have paired electrons are **diamagnetic**. A paramagnetic substance is characterised by its magnetic moment which is calculated by 'spin only' formula, i.e.

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

where, n is the number of unpaired electrons and BM is Bohr Magneton, the unit of magnetic moment.

A single unpaired electron has magnetic moment

$$\mu = \sqrt{1 \times (1+2)}$$
$$= 1.73\ \text{BM}$$

Magnetic moment increases with the increasing number of unpaired electrons. Substances which are attracted very strongly by a magnetic field and their domains are aligned in one direction are called **ferromagnetic substances**, e.g. Fe, Co, Ni. In fact, ferromagnetism is an extreme form of paramagnetism.

EXAMPLE |3| Calculate the magnetic moment of a divalent ion in aqueous solution, $[Fe(H_2O)_6]^{2+}$, if atomic number of Fe is 26.

Sol. Magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM

Atomic number of Fe $= 26 = [Ar]3d^6 4s^2$

$$Fe^{2+} = [Ar]3d^6 4s^0 = \boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$$

So, $\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.89$ BM

Formation of Coloured Ions

When an electron from a lower energy d-orbital is excited to a higher energy d-orbital, the energy of excitation corresponds to the frequency of light absorbed. This frequency generally lies in the visible region.

The colour observed corresponds to the complementary colour of the light absorbed. The frequency of light absorbed is determined by the nature of the ligand. Thus, most of the compounds of transition metals are coloured due to d-d transition. Transition metal ions having d^0 configuration are colourless.

When ligand has free electrons, the transfer of electron from anion to cation takes place. In this case, energy is absorbed during this process which is responsible for colour.

Note Few compounds in which transition metal has d^0 configuration, may also exhibit colour due to charge transfer. e.g. CrO_3 has d^0 configuration of Cr and shows orange colour due to charge transfer.

Formation of Complex Compounds

Complex compounds are those compounds in which the metal ions bind a number of anions or neutral molecules, giving characteristic properties to the complexes.

Transition metals form a large variety of complex compounds. e.g. $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[PtCl_4]^{2-}$ and $[Cu(NH_3)_4]^{2+}$, etc.

The transition metals form a large number of complex compounds due to the comparatively smaller size of the metal ions, their high charge density and vacant d-orbitals for bond formation.

Catalytic Properties

Many transition metals and their compounds are used as catalyst. Their catalytic activity is due to their ability to adopt multiple oxidation states and to form complexes. Transition metals because of their variable valencies sometimes form unstable intermediate compounds and provide a new path with lower activation energy for the reaction, e.g. V_2O_5 (contact process), finely divided iron (in Haber's process) and nickel (in catalytic hydrogenation).

Catalysts at a solid surface involve the bond formation between reactant molecules and atoms of the surface of catalyst. V_2O_5 catalyses the oxidation of SO_2 to SO_3 (contact process).

During conversion of SO_2 to SO_3, V_2O_5 absorbs SO_2 molecules on its surface and gives oxygen to it to form SO_3 and V_2O_4. V_2O_4 then reacts with oxygen to form V_2O_5. Similarly, iron (III) catalyses the reaction between iodide and persulphate ions.

$$2I^- + S_2O_8^{2-} \xrightarrow{\text{Fe (III)}} I_2 + 2SO_4^{2-}$$

Thus, catalytic action of iron (III) in this reaction is explained as follows:

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$
$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

Thus, Fe^{3+} oxidises I^- ions to iodine.

In some cases, transition metals provide a suitable surface for the reaction to take place. The reactants are adsorbed on the surface of the catalyst. This weakens the bonds between atoms in the reactant molecules.

Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms such as H, C, N etc. are trapped inside the crystal lattices of metals.

They are generally non-stoichiometric and are neither typically ionic nor covalent, e.g. Mn_4N, TiC, Fe_3H, $TiH_{1.7}$, $VH_{0.56}$, etc.

The formulas quoted do not correspond to any normal oxidation state of the metal. These compounds are hard (some borides approach diamond in hardness), chemically inert, metallic conductor and have high melting point than those of pure metals.

Alloy Formation

An alloy is a blend of metals prepared by mixing the components. An alloy is a homogeneous solid solution. Atoms of transition metal due to similar sizes, can easily take place in the crystal lattice of another metal in the molten state and are miscible with each other forming alloys. Alloys are generally hard, resistant to corrosion and have high melting point.

Ferrous alloys (with Cr, V, W, Mo and Mn), form varieties of steel, which are best of the class. Brass (Cu-Zn) and bronze (Cu-Sn) are the alloys of transition metals and have considerable industrial importance.

Note Alloys of mercury with metals are known as amalgams.

TOPIC PRACTICE 1

OBJECTIVE Type Questions

1. Electronic configuration of a transition element X in +3 oxidation state is $[Ar]3d^5$. What is its atomic number? **NCERT Exemplar**

(a) 25 (b) 26
(c) 27 (d) 24

2. The electronic configuration of Cu(II) is $3d^9$ whereas that of Cu(I) is $3d^{10}$. Which of the following is correct? **NCERT Exemplar**

(a) Cu(II) is more stable
(b) Cu(II) is less stable
(c) Cu(I) and Cu(II) are equally stable
(d) Stability of Cu(I) and Cu(II) depends on nature of copper salts

3. Metallic radii of some transition elements are given below. Which of these elements will have highest density?

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

NCERT Exemplar

(a) Fe (b) Ni (c) Co (d) Cu

4. Which of the following is the reason for zinc not exhibiting variable oxidation state? **CBSE SQP 2021**

(a) Inert pair effect
(b) Completely filled $3d$-subshell
(c) Completely filled $4s$-subshell
(d) Common ion effect

5. Which of the following statement is not correct? **NCERT Exemplar**

(a) Copper liberates hydrogen from acids
(b) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine
(c) Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution
(d) Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution

6. Highest oxidation state of manganese in fluoride is +4 (MnF_4) but highest oxidation state in oxides is +7(Mn_2O_7) because **NCERT Exemplar**

(a) fluorine is more electronegative than oxygen
(b) fluorine does not possess d orbitals
(c) fluorine stabilises lower oxidation state
(d) in covalent compounds, fluorine can form single bond only while oxygen forms double bond

7. Which of the following is a diamagnetic ion (atomic numbers of Sc, V, Mn and Cu are 21, 23, 25 and 29 respectively) **CBSE SQP 2021**

(a) V^{2+} (b) Sc^{3+}
(c) Cu^{2+} (d) Mn^{3+}

8. The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment. **NCERT Exemplar**

(a) $3d^7$ (b) $3d^5$
(c) $3d^8$ (d) $3d^2$

9. Which set of ions exhibit specific colours ? (Atomic number of Sc = 21, Ti = 22, V = 23, Mn = 25, Fe = 26, Ni = 28 , Cu = 29 and Zn = 30) **CBSE SQP 2021**

(a) Sc^{3+}, Ti^{4+}, Mn^{3+} (b) Sc^{3+}, Zn^{2+}, Ni^{2+}
(c) V^{3+}, V^{2+}, Fe^{3+} (d) Ti^{3+}, Ti^{4+}, Ni^{2+}

10. Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds? **All India 2020, NCERT Exemplar**

(a) They have high melting points in comparison to pure metals
(b) They are very hard
(c) They retain metallic conductivity
(d) The are chemically very reactive

VERY SHORT ANSWER Type Questions

11. Write down the general electronic configuration of transition elements.

12. Transition metals and their compounds show catalytic activities. **Delhi 2020**

13. Silver atom has completely filled d-orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element? **NCERT Intext**

14. In the series Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomisation of zinc is lowest, i.e. 126 kJ mol^{-1}. Why? **NCERT Intext**

15. Which transition metal of the $3d$-series exhibits the largest number of oxidation states and why? **NCERT Intext, All India 2014**

16. The second and third rows of transition elements resemble each other much more than they resemble the first row. Why? **NCERT Exemplar**

17. Zn, Cd and Hg are soft and have low melting point. **Delhi 2020**

18. The $E^\circ_{M^{2+}/M}$ value of copper is positive (+ 0.34 V). What is the possible reason for this? **All India 2012**

Or Which transition metal of the 3*d*-series has positive $E^\circ_{M^{2+}/M}$ value and why? **All India 2014**

19. Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state? **NCERT**

20. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only? **NCERT Intext**

SHORT ANSWER Type I Questions

21. What are the transition elements? Write the two characteristics of the transition elements. **Delhi 2015**

22. Name the two transition elements which have abnormal electronic configuration and why?

23. Write down the electronic configuration of
(i) Cr^{3+} (ii) Cu^{+} (iii) Co^{2+} (iv) Mn^{2+} **NCERT**

24. Explain the following observations:
(i) Copper atom has completely filled *d*-orbitals ($3d^{10}$) in its ground state, yet it is regarded as a transition element.
(ii) Cr^{2+} is a stronger reducing agent than Fe^{2+} in aqueous solutions.
Delhi 2020, All India 2020, 2017 C

25. Explain, why density of transition elements increases from left to right in a period?

26. Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number. **NCERT**

27. Explain briefly how + 2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number? **NCERT**

Or Compare the stability of + 2 oxidation state for the elements of the first transition series. **NCERT**

28. Explain, why oxidation states of transition elements first increases from Sc to Mn and then decreases?

29. Which metal in the first series of transition metals exhibit + 1 oxidation state most frequently and why? **Delhi 2013; NCERT**

30. Why E° values for Mn, Ni and Zn are more negative than expected? **NCERT Exemplar**

31. For the first row transition metals, the E° values are given below:

Elements	V	Cr	Mn	Fe	Co	Ni	Cu
$E^\circ_{M^{2+}/M}$	−1.18	− 0.91	−1.18	−0.44	−0.28	− 0.25	+0.34

Explain the irregularity in the above values. **All India 2013**

32. Explain why Cu^{+} ion is not stable in aqueous solution? **NCERT Intext**

Or Explain why Cu (I) ion is not known in aqueous solution? **All India 2020, 2013**

33. Calculate the 'spin only' magnetic moment of $M^{2+}(aq)$ ion. (Z = 27) **NCERT Intext**

34. Predict which of the following will be coloured in aqueous solution?
Ti^{3+}, V^{3+}, Cu^{+}, Sc^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+}. Give reasons for each. **NCERT; Delhi 2013**

SHORT ANSWER Type II Questions

35. Calculate the number of unpaired electrons in the following gaseous ions Mn^{3+}, Cr^{3+}, V^{3+} and Ti^{3+}. Which one of these is the most stable in aqueous solution? **NCERT**

36. The halides of transition elements become more covalent with increasing oxidation state of the metal. Why? **NCERT Exemplar**

37. Why do transition elements show variable oxidation states?
(i) Name the element showing maximum number of oxidation states among the first series of transition metals from Sc (Z = 21) to Zn (Z = 30).
(ii) Name the element which shows only +3 oxidation state. **All India 2013**

38. Ni^{2+} is more stable than Pt^{2+} but the trend is reverse where Pt^{4+} is more stable than Ni^{4+}. Explain.

39. Give reasons for the following.
(i) Mn^{3+} is a good oxidising agent. **All India 2020**

(ii) $E^\circ_{M^{2+}/M}$ values are not regular for first row of transition metals (3*d*-series).

(iii) Although F is more electronegative than O, the highest fluoride of Mn is MnF_4, whereas the highest oxide is Mn_2O_7. **All India 2013**

40. How would you account for the following?

(i) Of the d^4 species, Cr^{2+} is strongly reducing agent while manganese (III) is strongly oxidising agent.

(ii) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents, it is easily oxidised.

(iii) The d^1 configuration is very unstable in ions. **NCERT**

41. Observed and calculated values for the standard electrode potentials of elements from Ti to Zn in the first reactivity series are depicted in figure (Refer to page 140): **CBSE SQP 2021**

Explain the following observations :

(i) The general trend towards less negative E° values across the series.

(ii) The unique behaviour of copper.

(iii) More negative E° values of Mn and Zn.

42. Give reasons:

(a) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+}.

(b) Iron has higher enthalpy of atomisation than that of copper.

(c) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is colured. **CBSE 2018**

43. Account for the following.

(i) Ti(IV) is more stable than the Ti (II) or Ti(III).

(ii) In case of transition elements, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number.

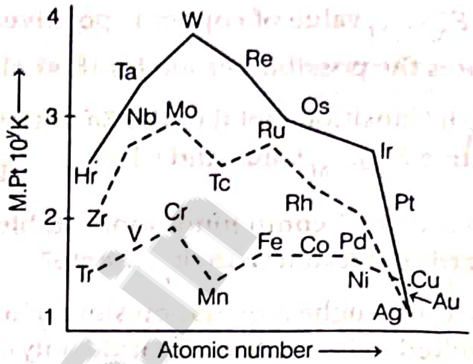
(iii) Zinc is comparatively a soft metal, iron and chromium are typically hard. **CBSE SQP (Term II)**

44. (i) Why are fluorides of transition metals more stable in their higher oxidation state as compared to the lower oxidation state? **CBSE SQP (Term II)**

(ii) Which one of the following would feel attraction when placed in magnetic field Co^{2+}, Ag^+, Ti^{4+} and Zn^{2+}?

(iii) It has been observed that first ionisation energy of 5*d*-series of transition elements are higher than that of 3*d* and 4*d* series, explain why?

Or On the basis of the figure given below, answer the following questions:



(i) Why manganese has lower melting point than chromium?

(ii) Why do transition metals of 3*d*-series have lower melting point as compared to 4*d*-series?

(iii) In the third transition series, identify and name the metal with the highest melting point.

LONG ANSWER Type Questions

45. What are the characteristics of the transition elements and why are they called transition elements? Which of the *d*-block elements may not be regarded as the transition elements? **NCERT**

46. Explain giving reasons.

(i) The enthalpies of atomisation of the transition metals are high.

(ii) Transition metals and many of their compounds show paramagnetic behaviour.

(iii) The transition metals generally form coloured compounds.

(iv) Transition metals and their many compounds act as good catalyst. **NCERT; Delhi 2013**

47. Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points.

(i) Electronic configuration

(ii) Oxidation states

(iii) Ionisation enthalpies

(iv) Atomic size **NCERT**

48. Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements. **NCERT**

49. What can be inferred from the magnetic moment values of the following complex species?

Examples	Magnetic moment (BM)
$K_4[Mn(CN)_6]$	2.2
$[Fe(H_2O)_6]^{2+}$	5.3

NCERT

50. Write down the number of $3d$-electron in each of the following ions; Ti^{2+}, V^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}.

Indicate how would you expect the five $3d$-orbitals to be occupied for these hydrated ions (octahedral)?

NCERT

HINTS AND EXPLANATIONS

1. *(b)* Electronic configuration of X^{3+} is $[Ar]3d^5$

It repersents the total number of electrons and oxidation state.

Therefore, atomic number of $X = 18 + 5 + 3 = 26$

Hence, option (b) is correct.

2. *(a)* Cu(II) is more stable than Cu(I).

As it is known that, Cu(I) has $3d^{10}$ stable configuration while Cu(II) has $3d^9$ configuration.

But Cu(II) is more stable due to greater effective nuclear charge of Cu(II) i.e., it hold 17 electrons instead of 18 in Cu(I).

3. *(d)* On moving left to right along period, metallic radius decreases while atomic mass increases. Decrease in metallic radius coupled with increase in atomic mass results in increase in density of metal.

Hence, among the given four choices Cu belongs to right side of Periodic Table in transition metal, and it has highest density (89 g/cm^3).

4. *(b)* Zinc does not exhibit variable oxidation state due to the completely filled $3d$-subshell.

The orbitals in these elements are completely filled in the ground state as well as in their oxidation state. These do not show any characteristic properties of transition elements except complex formation.

5. *(a)* Copper lies below hydrogen in the electrochemical series and hence does not liberate H_2 from acids. Therefore, option (a) is not correct.

Other three options (b, c, d) are correct.

6. *(d)* Highest oxidation state of manganese in fluoride is +4 (MnF_4) but highest oxidation state in oxides is +7(Mn_2O_7).

The reason is that in covalent compounds fluorine can form single bond while oxygen forms double bond.

7. *(b)* Sc^{3+} is a diamagnetic ion whereas V^{2+}, Cu^{2+} and Mn^{3+} are paramagnetic in nature. These are shown below:

Ion	Electronic configuration	Unpaired electrons	Nature
Sc^{3+}	$3d^0$	0	Diamagnetic
V^{2+}	$3d^3$	3	Paramagnetic
Cu^{2+}	$3d^9$	1	Paramagnetic
Mn^{3+}	$3d^4$	4	Paramagnetic

8. *(b)* Greater the number of unpaired electron, higher will be its value of magnetic moment.

Since, $3d^5$ has 5 unpaired electrons hence highest magnetic moment.

$$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.95 \text{BM}$$

9. *(c)* V^{3+}, V^{2+} and Fe^{3+} exhibit colours due to d-d transition. Transition metal ion having d^0 and d^{10}-configuration are colourless as d-d transition is not possible.

$$V^{3+}(3d^2) \longrightarrow \text{Green}$$
$$V^{2+}(3d^3) \longrightarrow \text{Violet}$$
$$Fe^{3+}(3d^6) \longrightarrow \text{Green}$$

10. *(d)* Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals.

Some of their important characteristics are as follows

(i) They are very hard and rigid.

(ii) They have high melting point which are higher than those of the pure metals.

(iii) They show conductivity like that of the pure metal.

(iv) They acquire chemical inertness.

11. $(n-1)d^{1-10}ns^{1-2}$.

12. Refer to page 143 (Catalytic properties).

13. Silver in its +1 oxidation state, exhibits $4d^{10}\,5s^0$ configuration. But in some compounds, it also shows +2 oxidation state, so the configuration becomes $4d^9\,5s^0$. Here, d-orbital is not completely filled. Therefore, silver is a transition element.

14. Zinc has stable ground state due to its completely filled d-orbitals. It therefore, has least tendency to form metallic bonds, in the series, thus requires least enthalpy of atomisation to get atomised.

15. Manganese shows maximum number of oxidation states (EC : $3d^5, 4s^2$), i.e. + 2, + 3, + 4, + 5, + 6, + 7 in its compounds due to maximum number of unpaired electrons.

16. Due to lanthanoid contraction, the atomic radii of the second and third rows of transition elements is almost same. So, they resemble each other much more as compared to first row elements and show similar characteristics.

17. Zn, Cd and Hg are generally soft and have low melting point because all the electrons in their d-orbital are paired. Hence, the metallic bonds which are present in them are weak.

18. $E^{\circ}_{M^{2+}/M}$ value of copper is positive as value of hydration enthalpy is less than the sum of values of ionisation enthalpy and enthalpy of ionisation.

19. Mn^{2+} compounds are more stable due to half-filled d-orbitals. Fe^{2+}compounds are comparatively less stable as they have six electrons in their orbitals.

So, they tend to lose one electron from Fe^{2+} and get stable $3d^5$configuration.

20. Oxygen and fluorine both have small size and high value of electronegativity. So, they can oxidise the metal to their highest oxidation states.

21. Refer to text on pages 136 and 137.

22. **Hint** Cu and Cr Refer to text on page 137.

23. Electronic configuration of the given ions are :

(i) $Cr^{3+} (Z = 24) = 1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6 3d^3$

Here, $1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6$ refers to the electronic configuration of $[Ar]^{18}$, thus electronic configuration of Cr^{3+} can be written as:

$Cr^{3+} = [Ar]\ 3d^3$.

For (ii), (iii) and (iv) Refer to table on page 136.

24. (i) Because it has incompletely filled d-orbitals in one of its oxidation states i.e. Cu^{2+} ($[Ar]3d^9$).

(ii) Cr^{2+}($[Ar]\ 3d^4$) changes to Cr^{3+} ($[Ar]\,3d^3$) while Fe^{2+} ($[Ar]3d^6$) changes to Fe^{3+} ($[Ar]\ 3d^5$).

In aqueous medium, the configuration $[Ar]\ 3d^3$ is more stable than the configuration $[Ar]\ 3d^5$. Hence, Cr^{2+} is a stronger reducing agent.

25. While going from left to right in a period, the radii of transition metals remains similar but their atomic masses increases gradually. As a result their density increases correspondingly.

26. $[ScO_2]^-$: Group number = Oxidation state of Sc = 3

$[TiO_3]^{2-}$: Group number = Oxidation state of Ti = 4

$[VO_3]^-$: Group number = Oxidation state of V = 5

$[Cr_2O_7]^{2-}$: Group number = Oxidation state of Cr = 6

$[CrO_4]^{2-}$: Group number = Oxidation state of Cr = 6

$[MnO_4]^-$: Group number = Oxidation state of Mn = 7

27. Elements (+ 2 state) ${}_{21}Sc^{2+}, {}_{22}Ti^{2+}, {}_{23}V^{2+}, {}_{24}Cr^{2+}$ and ${}_{25}Mn^{2+}$ have more stable +2 oxidation state and the outer electronic configuration are $3d^1, 3d^2, 3d^3, 3d^4$ and $3d^5$, respectively. In all the elements listed, the removal of two $4s$ electrons (in Cr^{2+}, $1e^-$ from $4s$ and $1e^-$ from $3d$), the $3d$-orbitals get gradually occupied. Since, the number of empty d-orbitals decreases or the number of unpaired electrons in $3d$-orbitals increases with increase in atomic number of cations, so the stability of the cations (M^{2+}) increases from Sc^{2+} to Mn^{2+}.

28. The use of $3d$ electron for formation of bond increases from Sc to Mn, causing the increase in oxidation state up to +7. The reason for Mn having highest oxidation state of +7 is due to the presence of 7 unpaired electrons in its atom. As the number of unpaired electrons decreases from Fe to Cu so there is the decrease in oxidation state.

29. Electronic configuration of Cu is $[Ar]\,3d^{10}4s^1$. When copper atom loses 1 electron, it exhibits + 1 oxidation state and forms Cu^+ ion with stable $3d^{10}$ configuration. So, copper metal in the first transition series tends to have +1 oxidation state to achieve a stable configuration.

30. Negative values of Mn^{2+} and Zn^{2+} are related to stabilities of half-filled and completely filled configuration respectively. But for Ni^{2+}, E° value is related to the highest negative enthalpy of hydration.

Hence, E° values of Mn, Ni and Zn are more negative than expected.

31. It is due to irregular variation of sublimation enthalpies and ionisation enthalpies for elements of $3d$ transition series.

32. In aqueous solution, copper (I) undergoes disproportionation reaction.

$$2Cu^+ (aq) \longrightarrow Cu^{2+} + Cu(s)$$

The highest stability of Cu^{2+} ion in aqueous solution is due to negative enthalpy of hydration.

Hence, Cu^+ is not known (or unstable) in aqueous solution.

33. $\mu = 3.87$ BM

[Same method as example 3 on page 143.]

34. **Hint** Ions having d^0 configuration are colourless.

Refer to text on page 143.

35. $Mn^{3+} (Z = 25) = [Ar]\,3d^4$ [1|1|1|1|]

$Cr^{3+} (Z = 24) = [Ar]\,3d^3$ [1|1|1| |]

$V^{3+} (Z = 23) = [Ar]\,3d^2$ [1|1| | |]

$Ti^{3+} (Z = 22) = [Ar]\,3d^1$ [1| | | |]

Cr^{3+} is the most stable among these in aqueous solution because it has half-filled t_{2g} level ($= t^3_{2g}$).

36. This problem is based on the concept of Fajans' rule. As the oxidation state increases, size of the ion of transition element decreases. As per Fajans' rule, when the size of

metal ion decreases, covalent character of the bond formed increases.

Therefore, the halide of transition elements become more covalent with increasing oxidation state of the metal.

37. Transition elements show variable oxidation state due to their ability of utilising single or multiple 4s and 3d electrons.

(i) Mn (manganese) shows the maximum number of oxidation states.

(ii) Scandium shows only +3 oxidation state

38. Ni^{2+} compounds have the sum of first two ionisation enthalpies to be lower than that of Pt^{2+} compounds and are thermodynamically stable. However, the sum of first four IEs of Pt^{4+} is lower than that of first four IEs of Ni^{4+} and is relatively stable.

39. (i) Mn^{3+}/Mn^{2+} has large positive $E°$ value. Hence, Mn^{3+} can be easily reduced to Mn^{2+} because Mn^{2+} has half-filled electronic configuration, so it is stable and Mn^{3+} is least stable. Therefore, it is a good oxidising agent.

(ii) There is decreasing negative electrode potentials of M^{2+}/M in the first transition series due to increase in the sum of IE_1 and IE_2. It shows that in general, the stability of +2 oxidation state decreases from left to right. Exceptions are Mn and Zn in which the greater stability of +2 state for Mn is due to half-filled d-subshell (d^5) in Mn^{2+} and that of Zn is due to completely filled d-subshell (d^{10}) in Zn^{2+}.

(iii) It is because oxygen can form multiple bonds, whereas fluorine can only form single bonds with metals.

40. (i) $E°$ value of Cr^{3+}/Cr^{2+} is negative (– 0.41 V) while that of Mn^{3+}/Mn^{2+} is positive (+ 1.57 V). This means that Cr^{2+} ions can lose electrons to form Cr^{3+} ions and acts as a reducing agent while Mn^{3+} ions can accept electrons and can act as an oxidising agent.

(ii) Cobalt (III) ion has greater tendency to form complexes than cobalt (II) ion. Therefore, Co (II) ion being stable in aqueous solution, changes to Co (III) ion in the presence of complexing reagents and gets oxidised.

(iii) Ions of transition metals with d^1 configuration tend to lose one electron to acquire d^0 configuration that is quite stable. Therefore, such ions (with d^1) undergo either oxidation or disproportionation, hence unstable.

41. (i) The general trend towards less negative $E°$ V values across the series is related to the general increase in the sum of the first and second ionisation enthalpies.

(ii) The high energy to transform Cu(s) to Cu^{2+} (aq) is not balanced by its hydration enthalpy.

Most of Cu (I) compound are unstable in aqueous solution and undergo disproportionation.

$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$

(iii) The stability of the half-filled d-subshell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} are related to their more negative $E°$V values.

42. (a) Mn^{2+} compounds are more stable due to half-filled d-orbitals. Fe^{2+}compounds are comparatively less stable as they have six electrons in their orbitals. So, they tend to lose one electron from Fe^{2+} and get stable $3d^5$-configuration in Fe^{3+}.

Therefore, comparatively high positive value of $E°$ for Mn^{3+}/Mn^{2+}indicates the stability of $Mn^{2+}(d^5)$ whereas comparatively low value for Fe^{3+}/Fe^{2+} indicates the extra stability of $Fe^{3+}(d^5)$.

(b) Energy required to convert metallic crystal into individual atom is **enthalpy of atomisation.** In transition row elements it first increases and reaches to maximum upto middle element and then decreases. This is because of strong inter atomic interaction due to unpaired electron.

Greater the number of unpaired electron, stronger will be bonding and thus enthalpy of atomisation will also be more. Since iron has more unpaired electron than copper therefore its enthalpy of atomisation is more.

(c) The metal ions with partially or incomplete filled d-orbitals will be coloured in aqueous solution. While the metal ions having either empty or completely filled d-orbitals are colourless.

The colour will be due to d-d transition of electrons. Thus, the outer electronic configuration of metal ions are Sc^{3+} : $3d^0$, Ti^{3+}: $3d^1$

Hence, among the given ions, Ti^{3+} will exhibit colour in aqueous solution while Sc^{3+} will be colourless.

43. (i) Electronic configuration of Ti : $[Ar]3d^2 4s^2$

Electronic configuration of Ti^{4+} is [Ar]. It is stable noble gas configuration.

Electronic configuration of Ti^{2+} $[Ar]3d^2$

Electronic configuration of Ti^{3+} : $[Ar]3d^1$

As Ti^{4+} acquires nearest noble gas configuration on loss of 4 electrons, thus it is more stable than the Ti^{3+} and Ti^{2+}.

(ii) In case of transition elements, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number.

As with increase in atomic number, the new electron enters in d-orbitals and expected to increase in atomic size, but due to poor shielding effect of d- orbitals, the electrostatic attraction between nucleus and outermost orbital increases and hence, the ionic radii decreases.

(iii) Zinc is a soft metal as compared to iron and chromium because it has low enthalpy of atomisation (due to the absence of unpaired electron), whereas,

iron and chromium have high enthalpy of atomisation (due to the presence of unpaired electrons), which account for their hardness.

44. (i) Since, fluorine has smaller atomic size and higher electronegativity, therefore, it oxidises the metal to their higher oxidation state (due to higher lattice energy).

(ii) Electronic configuration of Co^{2+} : $[Ar]3d^7$

$$= \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$$

$3d^7$

It has three unpaired electrons.

Electronic configuration of Ag^+ : $[Kr]4d^{10}5s^0$

$$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$$

It does not have any unpaired electron.

Electronic configuration of Ti^{4+} : [Ar]

Unpaired electron is absent.

Electronic configuration of Zn^{2+} : [Kr]

Unpaired electron is absent.

Thus, since unpaired electron is present only in Co^{2+}, it is paramagnetic in nature, hence Co^{2+} ion would be attracted to magnetic field.

(iii) First ionisation energy of $5d$-series of transition elements are higher than that of $3d$ and $4d$-series because $5d$-series have intervening $4f$-orbitals.

There is greater effective nuclear charge acting on outer valence electrons due to the weak shielding by $4f$-electrons.

Therefore, large amount of energy is required to remove the outer electron in this case as compared to $3d$ and $4d$-series.

Or

(i) Manganese has lower melting point as compared to chromium because it has d^5 configuration, i.e. half-filled orbital.

It has highest unpaired electrons. These electrons are very less delocalised and can not help in effective metallic bonding.

(ii) There is less frequent metal-metal bonding in compounds of the $3d$-transition metal which is the main reason for its low melting point.

Heavy transition metal (i.e. $4d$ and $5d$-series) show more frequent metal-metal bond in their compounds.

(iii) Tungsten.

45. Refer to text on pages 136 and 137.

46. (i) Refer to text on page 138.

(ii) Refer to text on page 142.

(iii) Refer to text on page 143.

(iv) Refer to text on page 143.

47. (i) **Electronic configuration** The elements in the same vertical column generally have similar electronic configuration. Although, the first series has only two exceptions,

$$Cr = 3d^5\,4s^1 \text{ and } Cu = 3d^{10}4s^1$$

Second transition series have five exceptions,

$$Mo = 4d^5 5s^1,\ Nb = 4d^4 5s^1,$$

$$Rh = 4d^8 5s^1,\ Pd = 4d^{10}5s^0,\quad Ag = 4d^{10}5s^1$$

Third transition series has three exceptions,

$$W = 4f^{14}5d^4 6s^2,\quad Pt = 4f^{14}5d^9 6s^1$$

$$Au = 4f^{14}5d^{10}6s^1$$

(ii) **Oxidation states** Refer to text on pages 287 and 288.

(iii) **Ionisation enthalpies** The first ionisation enthalpy in each series generally increase gradually as we move from left to right. Though some exceptions are observed in each series.

The first ionisation enthalpies of some elements in the second ($4d$) series are higher, while some of them have lower value than the elements of $3d$-series in the same vertical column.

(iv) **Atomic size** Generally, ions of the same charge or atoms in a given series show progressive decrease in radius with increasing atomic number though the decrease is quite small.

But the size of the atoms of the $4d$-series is larger than the corresponding elements of the $3d$-series whereas those of corresponding elements of the $5d$-series are nearly the same as those of $4d$-series due to lanthanoid contraction.

48. The heavier transition elements belong to fourth ($4d$), fifth ($5d$) and sixth ($6d$) transition series. Their properties are expected to be different from the elements belonging to the first ($3d$) series due to the following reasons:

(i) Atomic radii of heavier transition elements ($4d$ and $5d$ series) are larger than those of the corresponding elements of the first transition series though those of $4d$ and $5d$-series are very close to each other.

(ii) Ionisation enthalpies of $5d$-series are higher than the corresponding elements of $3d$ and $4d$-series.

(iii) Enthalpies of atomisation of $4d$-and $5d$-series are higher than the corresponding elements of the first series.

(iv) Melting and boiling points of heavier transition elements are greater than those of the first transition series due to stronger intermetallic bonding.

(v) The elements of the first transition series generally form low spin or high spin complexes, depending upon the strength of ligand field. However, the heavier transition elements form low spin complexes irrespective of the strength of the ligand field.

49. Magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM

For $n = 1, \mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ BM ≈ 2

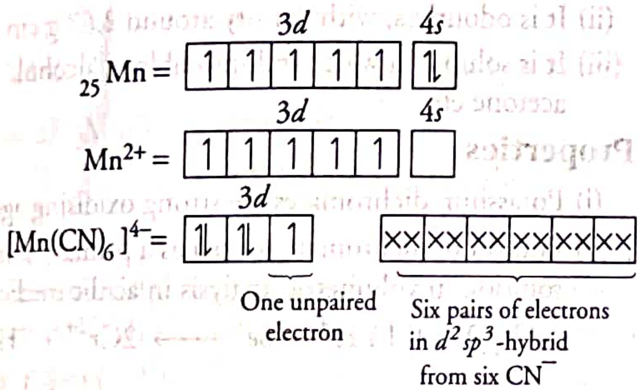
For $n = 2, \mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83$ BM ≈ 3

For $n = 3, \mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ BM ≈ 4

For $n = 4, \mu = \sqrt{4(4+2)} = \sqrt{24} = 4.90$ BM ≈ 5

For $n = 5, \mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92$ BM ≈ 6

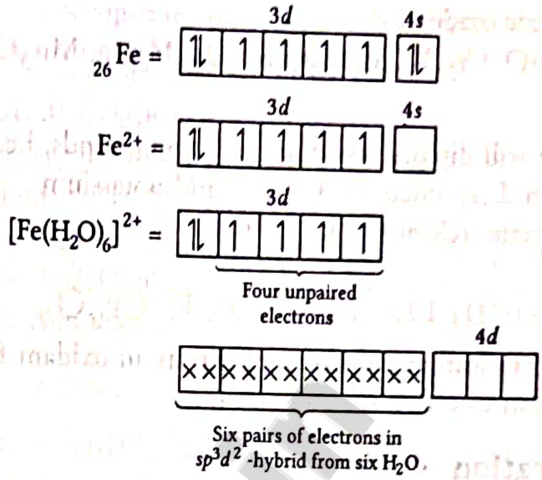
In $K_4[Mn(CN)_6]$, Mn is in +2 oxidation state, i.e. given value of μ (2.2 BM $\approx$ 2) indicates the presence of one unpaired electron. Since, CN^- is a strong field ligand. Hence, when CN^- ligands approach Mn^{2+} ion, the electrons in $3d$ pair up. Hybridisation involved is d^2sp^3 forming inner orbital octahedral complex.



In $[Fe(H_2O)_6]^{2+}$, Fe is in +2 oxidation state. Given, $\mu = 5.3$ BM (≈ 5), shows that there are four unpaired electrons. Since, H_2O is a weak ligand.

Hence, the electrons in 3d do not pair up when the ligands, i.e. H_2O molecules, approach.

To accommodate the electrons donated by H_2O molecules, the hybridisation is sp^3d^2. Hence, it will be an outer orbital octahedral complex.



50. All the ions form complex of the type $[M(H_2O)_6]^{n+}$. As water is a weak field ligand, therefore, in case of octahedral complex, pairing takes place, when each t_{2g} and e_g orbital is singly occupied [t_{2g} (d_{xy}, d_{yz}, d_{zx}) set is of lower energy and e_g ($d_{z^2}, d_{x^2-y^2}$) is of higher energy].

Ions	Configuration	Number of 3d electrons	Number of unpaired electrons	Occupancy of 3d-orbitals
Ti^{2+}	$3d^2$	2	2	t_{2g}^2
V^{2+}	$3d^3$	3	3	t_{2g}^3
Cr^{3+}	$3d^3$	3	3	t_{2g}^3
Mn^{2+}	$3d^5$	5	5	$t_{2g}^3e_g^2$
Fe^{2+}	$3d^6$	6	4	$t_{2g}^4e_g^2$
Fe^{3+}	$3d^5$	5	5	$t_{2g}^3e_g^2$
Co^{2+}	$3d^7$	7	3	$t_{2g}^5e_g^2$
Ni^{2+}	$3d^8$	8	2	$t_{2g}^6e_g^2$
Cu^{2+}	$3d^9$	9	1	$t_{2g}^6e_g^3$

TOPIC 2

Important Compounds and Applications of Transition Elements

OXIDES AND OXOANIONS OF METALS

Transition metals combine with oxygen at high temperature to give metallic oxides. Except scandium (Sc), all the metals upto Mn form monoxide (MO) which are ionic in nature. As oxidation number increases, covalent nature and acidic character increases while ionic character decreases. In general, the oxides in lower oxidation states of metals are basic and in their higher oxidation states, they are acidic, whereas in the intermediate oxidation state, the oxides are amphoteric.

Behaviour of oxides of manganese

$$\underset{\text{Basic}}{\overset{+2}{MnO}};\ \underbrace{\overset{+8/3}{Mn_3O_4}, \overset{+3}{Mn_2O_3}, \overset{+4}{MnO_2}}_{\text{Amphoteric}},\ \underset{\substack{\text{Acidic}\\ \text{(Covalent green oil)}}}{\overset{+7}{Mn_2O_7}}$$

Basic oxides Sc_2O_3, TiO, Ti_2O_3, VO, V_2O_3, MnO, FeO, CuO, CoO, NiO, Cu_2O, CrO

Acidic oxides Mn_2O_7, CrO_3, OsO_4

Amphoteric oxides
TiO_2, ZnO, Cr_2O_3, Mn_2O_3, MnO_2, V_2O_5, Mn_3O_4, Fe_3O_4

Here, we will discuss two important compounds, i.e. potassium dichromate ($K_2Cr_2O_7$) and potassium permangnate ($KMnO_4$) in details.

Potassium Dichromate, $K_2Cr_2O_7$

It is used in leather industry and acts as an oxidant for the preparation of many azo compounds.

Preparation

Potassium dichromate is prepared by chromite ore ($FeCr_2O_4$).

(i) When chromite ore is fused with sodium or potassium carbonate in free access of air.

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 2Fe_2O_3 + \underset{\text{Sodium chromate}}{8Na_2CrO_4} + 8CO_2$$

(ii) Yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give orange sodium dichromate solution.

$$2Na_2CrO_4 + 2H^+ \longrightarrow \underset{\substack{\text{Sodium dichromate}\\\text{(Orange)}}}{Na_2Cr_2O_7} + 2Na^+ + H_2O$$

$K_2Cr_2O_7$ is prepared by treating the solution of $Na_2Cr_2O_7$ with KCl because sodium dichromate is more soluble than potassium dichromate.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{\substack{\text{Potassium}\\\text{dichromate}}}{K_2Cr_2O_7} + 2NaCl$$

Orange coloured crystals of $K_2Cr_2O_7$ separates out.

In the solution, chromate ions exist in equilibrium with dichromate ions.

Depending on the pH of solution, equilibrium shifts in the forward and backward direction.

The oxidation state of chromium in chromate and dichromate ion is same.

In alkaline medium,

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

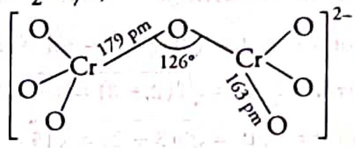
In acidic medium,

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

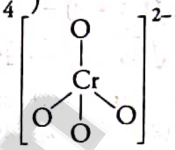
Structure

The structure of chromate ion (CrO_4^{2-}) is tetrahedral and dichromate ion ($Cr_2O_7^{2-}$) consists of two tetrahedral sharing one corner with Cr—O—Cr bond angle of 126°.

Dichromate ion ($Cr_2O_7^{2-}$)



Chromate ion (CrO_4^{2-})



Physical Properties

(i) It is a crystalline ionic solid having bright, reddish-orange colour.

(ii) It is odourless, with density around 2.67 g cm^{-3}.

(iii) It is soluble in water and insoluble in alcohol, acetone etc.

Properties

(i) Potassium dichromates are strong oxidising agents.

(ii) Potassium dichromate is used as a primary standard solution in volumetric analysis in acidic medium,

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \quad (E^\circ = 1.33\text{ V})$$

Thus, acidified potassium dichromate oxidises iodides to iodine, sulphides to sulphur, iron (II) salts to
iron (III) and tin (II) to tin (IV).

$$6I^- \longrightarrow 3I_2 + 6e^-$$
$$3H_2S \longrightarrow 6H^+ + 3S + 6e^-$$
$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$$
$$3Sn^{2+} \longrightarrow 3Sn^{4+} + 6e^-$$

The full ionic equation may be obtained by adding half reaction for potassium dichromate ($K_2Cr_2O_7$) to half reaction for reducing agent.

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

(iii) $Cr_2O_7^{2-}$ oxidises nitrites, NO_2^- to nitrates, NO_3^-

$$Cr_2O_7^{2-} + 8H^+ + 3NO_2^- \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$

Note Sodium dichromate, like potassium dichromate, is also an excellent oxidising agent and it being highly water soluble is extensively used as an oxidising agent in organic chemistry.

Uses

It is used as an oxidising agent, disinfectant, in volumetric analysis, for tanning of leather and in chromyl chloride test.

Potassium Permanganate, $KMnO_4$

It is a powerful oxidising agent in solution state and acts as a strong bleaching agent.

Preparation

(i) Potassium permanganate is prepared by pyrolusite (MnO_2) ore. When pyrolusite ore is fused with alkali metal hydroxide in the presence of air or an oxidising agent like KNO_3, potassium manganate is formed.

$$2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{Potassium manganate}}{2K_2MnO_4} + 2H_2O$$

Potassium manganate (K_2MnO_4) is of green colour which disproportionate in a neutral or acidic solution to produce potassium permanganate.

$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

or $3K_2MnO_4 + 4H^+ \longrightarrow$

$$\underset{\text{Potassium permanganate}}{2KMnO_4} + MnO_2 + 2H_2O + 4K^+$$

(ii) Commercially, it is prepared by alkaline oxidative fusion of MnO_2 followed by electrolytic oxidation of manganate (VI).

$$MnO_2 \xrightarrow[\text{Oxidised with air or } KNO_3]{\text{Fused with KOH}} \underset{\text{Manganate ion}}{MnO_4^{2-}}$$

$$MnO_4^{2-} \xrightarrow[\text{in alkaline solution}]{\text{Electrolytic oxidation}} \underset{\text{Permanganate ion}}{MnO_4^-}$$

(iii) In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

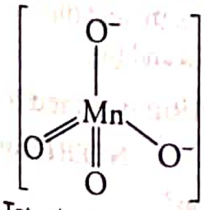
$$MnO_4^{2-} \longrightarrow MnO_4^- + e^-$$

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

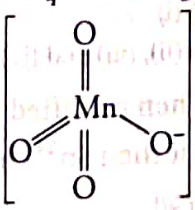
Dark purple crystals are formed which are isostructural with $KClO_4$.

Structure

The manganate, MnO_4^{2-} and permanganate, MnO_4^- are tetrahedral, the green MnO_4^{2-} is paramagnetic with one unpaired electron but the purple MnO_4^- is diamagnetic.



Tetrahedral manganate ion (green) (Paramagnetic)



Tetrahedral permanganate ion (purple) (Diamagnetic)

The π-bonding takes place by overlapping of p-orbitals of oxygen with d-orbitals of manganese.

Physical Properties

(i) It is dark purple coloured (the deep purple colour of $KMnO_4$ is due to charge transfer from O to Mn) crystalline solid. It is moderately soluble in water (6.4 g/100 g of H_2O at 293 K). On heating, it decomposes at 513 K and O_2 is evolved.

$$2KMnO_4 \xrightarrow{513\text{ K}} K_2MnO_4 + MnO_2 + O_2$$

(ii) It is stored in dark coloured bottles because it gets decomposed in the presence of sunlight.

(iii) It has weak paramagnetism which depends upon temperature.

Chemical Properties

Potassium permanganate ($KMnO_4$) produces nascent oxygen in solution state, which is the cause of its bleaching and oxidising properties. Its important reactions are as follows :

Bleaching Action of $KMnO_4$ in Different Solution

(i) Neutral solution

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

(ii) Alkaline solution

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$$

(iii) Acidic solution

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

Oxidation Reactions of Acidified $KMnO_4$

(i) Iodide to iodine

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$[2I^- \longrightarrow I_2 + 2e^-] \times 5$$

$$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

(ii) Ferrous to ferric

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$[\underset{\text{(Green)}}{Fe^{2+}} \longrightarrow \underset{\text{(Yellow)}}{Fe^{3+}} + e^-] \times 5$$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(iii) **Oxalate to carbon dioxide** (at 333 K)

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$
$$\overline{2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$$

(iv) **Hydrogen sulphide to sulphur**

$$H_2S \longrightarrow 2H^+ + S^{2-}$$
$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[S^{2-} \longrightarrow S + 2e^-] \times 5$$
$$\overline{2MnO_4^- + 5S^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 5S + 8H_2O}$$

(v) **Sulphurous acid or sulphite to sulphate or sulphuric acid**

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5$$
$$\overline{5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O}$$

(vi) **Nitrite to nitrate**

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-] \times 5$$
$$\overline{2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O}$$

Oxidation Reaction of Neutral or Mildly Alkaline $KMnO_4$

(i) **Iodide to iodate**

$$[MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-] \times 2$$
$$I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$$
$$\overline{2MnO_4^- + I^- + H_2O \longrightarrow IO_3^- + 2MnO_2 + 2OH^-}$$

(ii) **Thiosulphate to sulphate**

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

(iii) **Manganous salt to MnO_2**

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \xrightarrow{ZnO \text{ or } ZnSO_4} 5MnO_2 + 4H^+$$

Uses

In analytical chemistry, it is used as an oxidant in the preparation of organic compounds, bleaching of wool, cotton, silk, decolourisation of oils (Volumetric titrations involving $KMnO_4$ are carried out only in the presence of dil. H_2SO_4). In case HCl is used, it is oxidised to Cl_2 and in cleaning surgical instruments in hospitals.

APPLICATIONS OF TRANSITION METALS

(i) Iron and steel are the most important construction materials.
(ii) TiO is used in pigment industry.
(iii) MnO_2, Zn, Ni and Cd are used in battery industries.
(iv) Cu, Ag and Au are used for making coins and ornaments.
(v) V_2O_5 is used as a catalyst in the manufacture of sulphuric acid.
(vi) $TiCl_4$ with $Al(CH_3)_3$ is used in the manufacture of polythene.
(vii) Iron catalyst is used in Haber's process for the manufacture of ammonia.
(viii) Ni catalyst is used for hydrogenation of fats.
(ix) Light sensitive properties of AgBr are used in photographic industries.
(x) Steel, titanium nitride, titanium carbide, etc., are used for making artificial joint replacement of bones.

TOPIC PRACTICE 2

OBJECTIVE Type Questions

1. Which of the following compounds is used as the starting material for the preparation of potassium dichromate?
   (a) $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ (chrome alum)
   (b) $PbCrO_4$ (chromite yellow)
   (c) $FeCr_2O_4$ (chromite)
   (d) $PbCrO_4 \cdot PbO$ (chrome red)

2. Which of the following reactions are disproportionation reactions? **NCERT Exemplar**
   (i) $Cu^+ \longrightarrow Cu^{2+} + Cu$
   (ii) $3MnO_4^- + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$
   (iii) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$
   (iv) $2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$
   (a) (i) (b) (i), (ii) and (iii)
   (c) (ii), (iii) and (iv) (d) (i) and (iv)

3. When acidified $K_2Cr_2O_7$ solution is added to Sn^{2+} salt then Sn^{2+} changes to **NCERT Exemplar**
   (a) Sn (b) Sn^{3+}
   (c) Sn^{4+} (d) Sn^+

4. The equilibrium, $Cr_2O_7^{2-} \rightleftharpoons 2CrO_4^{2-}$ is shifted to right in
(a) an acidic medium (b) a basic medium
(c) a neutral medium (d) it does not exist

5. $KMnO_4$ acts as an oxidising agent in acidic medium. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphide ions in acidic solution is **NCERT Exemplar**
(a) $\frac{2}{5}$ (b) $\frac{3}{5}$ (c) $\frac{4}{5}$ (d) $\frac{1}{5}$

6. Why is HCl not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium? **NCERT Exemplar**
(a) Both HCl and $KMnO_4$ act as oxidising agents
(b) $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent
(c) $KMnO_4$ is a weaker oxidising agent than HCl
(d) $KMnO_4$ acts as a reducing agent in the presence of HCl

7. $KMnO_4$ acts as an oxidising agent in alkaline medium. When alkaline $KMnO_4$ is treated with KI, iodide ion is oxidised to .... **NCERT Exemplar**
(a) I_2 (b) IO^-
(c) IO_3^- (d) IO_4^-

8. On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following. **NCERT Exemplar**
(a) Mn_2O_7 (b) MnO_2
(c) $MnSO_4$ (d) Mn_2O_3

9. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because **NCERT Exemplar**
(a) CO_2 is formed as the product
(b) reaction is exothermic
(c) MnO_4^- catalyses the reaction
(d) Mn^{2+} acts as autocatalyst

10. Catalyst used in the oxidsation of SO_2 in the manufacture of H_2SO_4 is
(a) $CuCl_2$
(b) V_2O_5
(c) MnO_2
(d) None of the above

VERY SHORT ANSWER Type Questions

11. Which of the following are amphoteric oxides? Mn_2O_7, CrO_3, Cr_2O_3, CrO, V_2O_5, V_2O_4

12. What happens when dichromate ion is dissolved in alkali?

13. Write the formula of compound in which transition metal is in +7 oxidation state.

14. Cr^{2+} is a strong reducing agent whereas Mn^{3+} with the same d^4 configuration is an oxidising agent. Explain.

15. What happens when $KMnO_4$ is treated with KI?

SHORT ANSWER Type I Questions

16. Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with (i) iodide (ii) iron (II) solution and (iii) H_2S. **NCERT**

17. Explain why does colour of $KMnO_4$ disappear when oxalic acid is added to its solution in acidic medium? **NCERT Exemplar**

18. Complete the following equations.
(i) $2CrO_4^{2-} + 2H^+ \longrightarrow$
(ii) $KMnO_4 \xrightarrow{\text{Heat}}$
All India 2013

19. $Cr_2O_7^{2-} \xrightarrow{H^+} Cr^{3+}$; $E°_{RP} = +1.33$ V
$MnO_4^- \xrightarrow{H^+} Mn^{2+}$; $E°_{RP} = +1.51$ V
What can you assert about the nature of $KMnO_4$ and $K_2Cr_2O_7$?

20. Complete and balance the following chemical equations: **CBSE 2018**
(a) $Fe^{2+} + MnO_4^- + H^+ \rightarrow$ (b) $MnO_4^- + H_2O + I^- \rightarrow$

SHORT ANSWER Type II Questions

21. Give reasons for the following: **CBSE SQP 2021**
(i) Transition elements act as catalysts.
(ii) It is difficult to obtain oxidation state greater than two for copper.
(iii) CrO is basic but Cr_2O_3 is amphoteric.

22. Describe the preparation of potassium dichromate from chromite ore. What is the effect of the increasing pH on a solution of potassium dichromate?
Delhi 2020, NCERT; All India 2019, 2012

23. Complete the following chemical equations.
(i) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow$
(ii) $2CrO_4^{2-} + 2H^+ \longrightarrow$
(iii) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow$
All India 2020, 2019, Delhi 2013

24. What happens when $KMnO_4$ reacts with H_2O
(i) in strong acidic medium?
(ii) in neutral medium?
(iii) in alkaline medium?

25. When orange solution containing $Cr_2O_7^{2-}$ ion is treated with an alkali, a yellow solution is formed and when H^+ ions are added to yellow solution, an orange solution is obtained. Explain, why does this happen?
NCERT Exemplar

26. A mixed oxide of iron and chromium is fused with sodium carbonate in free access of air to form a yellow coloured compound (*A*). On acidification, the compound (*A*) forms an orange coloured compound (*B*), which is a strong oxidising agent.

Identify compound (*A*) and (*B*). Write chemical reactions involved. **All India 2017C**

LONG ANSWER Type Questions

27. Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron (II) ions, (ii) SO_2 and (iii) oxalic acid?
Write the ionic equations for the reactions.
Delhi 2020, NCERT

28. (i) Name a compound of
(a) transition metal which is used in the manufacture of sulphuric acid.
(b) transition metal that is used in Haber's process for the manufacture of ammonia.
(c) transition metal that have light sensitive properties and act as valuable source in photographic industry.
(ii) Write the equations which are involved in the oxidation of hydrogen sulphide to sulphur by potassium permanganate solution.

29. When chromite ore is fused with sodium carbonate in free access of air and the product is dissolved in water, a yellow solution of compound (*A*) is obtained. On acidifying the yellow solution with sulphuric acid, compound (*B*) is crystallised out. When compound (*B*) is treated with KCl, orange crystals of compound (*C*) crystallise out. Identify (*A*), (*B*) and (*C*) and write the reactions involved. **Delhi 2017**

HINTS AND EXPLANATIONS

1. *(c)* Chromite is used as starting material for preparation of $K_2Cr_2O_7$.

2. *(a)* The reaction in which oxidation as well as reduction, occur upon same atom simultaneously is known as disproportionation reaction.

Oxidation

$$Cu^+ \longrightarrow Cu^{2+} + Cu$$

Reduction

3. *(c)* When acidified $K_2Cr_2O_7$ solution is added to Sn^{2+} salts then Sn^{2+} changes to Sn^{4+}.
The reaction is given below

Oxidation

$$\overset{+6}{Cr_2}O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} 3Sn^{4+} + 7H_2O$$

Reduction

4. *(b)* The equilibrium $Cr_2O_7^{2-} \rightleftharpoons 2CrO_4^{2-}$ is shifted to right in a basic medium.

5. *(a)* The reaction of $KMnO_4$ in which it acts as an oxidising agent in acidic medium is

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$H_2S + [O] \longrightarrow H_2O + S] \times 5$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$

5 moles of S^{2-} ions react with 2 moles of $KMnO_4$. So, 1 mole of S^{2-} ion will react with $\frac{2}{5}$ moles of $KMnO_4$.

6. *(b)* HCl is not used to make the medium acidic in oxidation reactions of $KMnO_4$ in acidic medium. The reason is that if HCl is used, the oxygen produced from $KMnO_4$ + HCl is partly utilised in oxidising HCl to Cl_2 which itself acts as an oxidising agent and partly oxidises the reducing agent.

7. (c) $KMnO_4$ acts as an oxidising agent in alkaline medium. When alkaline $KMnO_4$ is treated with KI, iodide ion is oxidised to IO_3^-.

Reaction $2KMnO_4 + H_2O + KI \longrightarrow 2MnO_4 + 2KOH + KIO_3$

or, $I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-$

8. (a) On addition of $KMnO_4$ to concentrated H_2SO_4, a green oily compound Mn_2O_7 is obtained which is highly explosive in nature.

$$2KMnO_4 + 2H_2SO_4(\text{Conc.}) \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

9. (d) When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because Mn^{2+} acts as autocatalyst.

Reduction half

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

Oxidation half

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$

Overall equation

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

End point of this reaction Colourless to light pink.

10. (b) V_2O_5 is used as catalyst in the oxidation of SO_2 in the manufacture of H_2SO_4.

11. V_2O_5 and Cr_2O_3 are amphoteric oxides because both react with alkalies as well as acids.

12. When dichromate ion is dissolved in alkali, it forms chromate ion.

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

13. $KMnO_4$, Mn has +7 oxidation state.

14. **Hint** $Cr^{3+} = t_{2g}^3\, e_g^0$ and $Mn^{2+} = t_{2g}^3\, e_g^2$

15. $2KMnO_4 + 2KI \longrightarrow 2MnO_2 + I_2 + 4KO$

$2KMnO_4 + KI + H_2O \longrightarrow KIO_3 + 2KOH + MnO_2$

16. Refer to text on pages 152 and 153.

17. When oxalic acid is added to acidic solution of $KMnO_4$, its colour disappear due to the reduction of MnO_4^- ion to Mn^{2+}. Chemical reaction occurring during this neutralisation reaction is as follows:

$$5C_2O_4^{2-} + \underset{\text{(Coloured)}}{2MnO_4^-} + 16H^+ \longrightarrow \underset{\text{(Colourless)}}{2Mn^{2+}} + 8H_2O + 10CO_2$$

18. (i) Refer to text on page 152.
(ii) Refer to text on page 153.

19. **Hint** Both $KMnO_4$ and $K_2Cr_2O_7$ acts as an oxidizing agents.

20. (a) $5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
(b) $2MnO_4^- + H_2O + I^- \longrightarrow IO_3^- + 2MnO_2 + 2OH^-$

21. (i) Many transition metals and their compounds are used as catalyst. Their catalytic activity is due to their ability to adopt multiple oxidation states and to form complexes.
Transition metals because of their variable valencies sometimes form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.
e.g. V_2O_5 (contact process), finely divided iron (in Haber's process) and nickel (in catalytic hydrogenation).
(ii) It is difficult to obtain oxidation state greater than two for copper due to high value of third ionisation enthalpy.
$Cu(29) = 3d^{10}4s^1$, $Cu^+ = 3d^{10}4s^0$, $Cu^{2+} = 3d^9 4s^0$
(iii) Oxidation state of Cr in CrO is +2, while that in Cr_2O_3 +3. As the oxidation number of a metal increases, its acidic character increases due to decrease in the size of the metal ion and increase in charge density.

22. Refer to text on page 152. **Hint** On increasing pH, $K_2Cr_2O_7$ changes into K_2CrO_4.

23. (i) Refer to text on page 152.
(ii) Refer to text on page 152.
(iii) Refer to text on page 154.

24. Refer to text on page 153.

25. When orange solution containing $Cr_2O_7^{2-}$ ion is treated with an alkali, a yellow solution of CrO_4^{2-} is obtained. In the same way, when H^+ ions are added to yellow solution, an orange solution is obtained due to interconversion.

$$\underset{\text{(Orange)}}{\underset{\text{Dichromate}}{Cr_2O_7^{2-}}} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\text{(Yellow)}}{\underset{\text{Chromate}}{CrO_4^{2-}}}$$

26. $A: Na_2CrO_4$; $B: Na_2Cr_2O_7$

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

27. Refer to text on pages 153 and 154.

28. (i) (a) Vanadium (b) Iron (c) Silver
(ii) **Hint** $2MnO_4^- + 5H_2S + 16H^+ \longrightarrow 2Mn^{2+} + 5S + 8H_2O$
Refer to text on page 152.

29. Compounds *A*, *B* and *C* are
$A: Na_2CrO_4$; $B: Na_2Cr_2O_7$; $C: K_2Cr_2O_7$
The reactions involved are as follows

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

|TOPIC 3| Inner-Transition Elements

Elements in which the last electron fill up in f-orbital are called f-block elements. These elements are also known as inner-transition elements. They have two series, i.e. lanthanoids (the 14 elements following lanthanum) and actinoids (the 14 elements following actinium).

Lanthanoids resemble one another more closely than do the members of ordinary elements in any series. They possess only one stable oxidation state and their chemistry provides an opportunity to study the effect of small changes in size and nuclear charge along a series of otherwise similar elements.

LANTHANOIDS

Properties of Lanthanoids

Some properties of lanthanoids are discussed below:

Electronic Configuration

General electronic configuration of lanthanoids are $6s^2 5d^{0-1} 4f^{1-14}$. In these elements, last electron enters into the $4f$-orbital till Yb($4f^{14}$). Only cerium, gadolinium and lutetium have electron in $5d$-orbital as well.

Electronic configurations and radii of lanthanum and lanthanoids

Atomic number	Name	Symbol	Outer electronic configurations Ln
57	Lanthanum	La	$5d^1 6s^2$
58	Cerium	Ce	$4f^1 5d^1 6s^2$
59	Praseodymium	Pr	$4f^3 6s^2$
60	Neodymium	Nd	$4f^4 6s^2$
61	Promethium	Pm	$4f^5 6s^2$
62	Samarium	Sm	$4f^6 6s^2$
63	Europium	Eu	$4f^7 6s^2$
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$
65	Terbium	Tb	$4f^9 6s^2$
66	Dysprosium	Dy	$4f^{10} 6s^2$
67	Holmium	Ho	$4f^{11} 6s^2$
68	Erbium	Er	$4f^{12} 6s^2$
69	Thulium	Tm	$4f^{13} 6s^2$
70	Ytterbium	Yb	$4f^{14} 6s^2$
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$

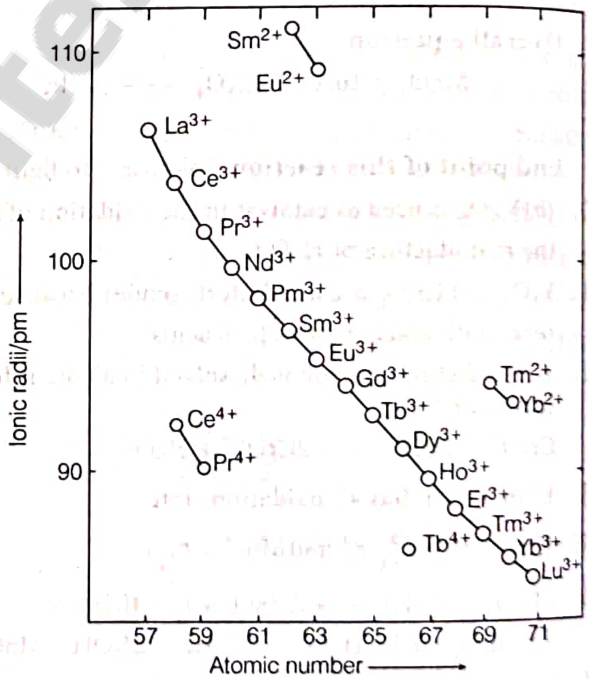
Atomic and Ionic Radii

The atomic and ionic radii decrease from lanthanum to lutetium. This is due to the unique property of lanthanoids which is known as lanthanoid contraction.

Lanthanoid Contraction

The filling of $4f$-orbital before $5d$-orbital results in a regular decrease in atomic radii called lanthanoid contraction. The factor responsible for the lanthanoid contraction is similar to that of ordinary transition series, i.e. the imperfect shielding of one electron by another in the same set of orbitals. However, the shielding of one $4f$-electron by another is less than that of one d-electron by another and as the nuclear charge increases along the series, there is fairly regular decrease in the size of the entire $4f^n$ orbitals.

The decrease in atomic radii is not regular but the decrease in ionic radii of their M^{3+} ions are quite regular as represented by the following graph.



Trends in ionic radii of lanthanoids

Consequences of Lanthanoid Contraction

(i) **Basic character of oxides and hydroxides** Due to the lanthanoid contraction, the covalent nature of Ln—OH bond increases as the basic character of oxides and hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$.

(ii) **Similarity in the size or radii of elements of second and third transition series** Because of lanthanoid contraction, elements which follow the third transition series are considerably smaller than that would otherwise be expected. The normal size increases from Sc → Y → La and disappears after lanthanoids. Thus, pairs of elements such as Zr/Hf, Nb/Ta and Mo/W are

almost identical in size. Due to almost similar size, such pairs have very similar properties which make their separation difficult and hence, also called chemical twin.

(iii) **Separation of lanthanoids** Due to lanthanoid contraction, there is a small difference in the size of lanthanoids. So, there is the difference in some properties of lanthanoids like solubility, degree of hydration and complex formation. These differences enable the separation of lanthanoids by ion exchange method.

Oxidation States

The most stable oxidation state of lanthanoids is +3. Oxidation states +2 and +4 also survive but they relapse to +3, e.g. Sm^{2+}, Eu^{2+} lose one electron to attain +3 state and hence are good reducing agents. Similarly, Yb^{2+} with f^{14} configuration acts as a reductant and Tb^{4+} with half-filled *f*-orbitals acts as an oxidant. While Ce^{4+}, Pr^{4+} in aqueous solution gain one electron to attain +3 state and hence are oxidising agents. There is a large gap in energy of $4f$- and $5d$-subshells and thus, the number of oxidation states is limited.

These are fourteen elements from cerium (Ce) to lutetium (Lu) as they closely resemble lanthanum. This is a $4f$-series. General trends in electronic configurations and radii of lanthanoids are tabulated below:

General Characteristics of Lanthanoids

(i) **Appearance** Lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number (samarium is steel hard).

(ii) **Density and melting point** Lanthanoids are highly dense metals and have high melting point (1000 to 1200 K). Sm has exceptionally high melting point of 1623 K.

(iii) **Metallic property** They have typical metallic structure and are good conductors of heat and electricity.

(iv) **Alloy formation** With other metals especially Fe they easily form alloys, e.g. alloy **mischmetal** of rare earth element (94%-95%), iron (upto 5%) and traces of S, C, Ca and Al. Pyrophoric alloys contain Ce (40.5%), La + neodymium (44%), Al, Ca and S.

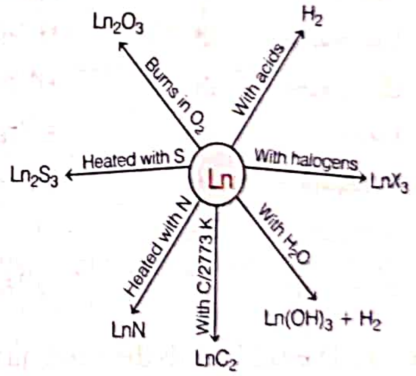
(v) **Magnetic properties** Generally, paramagnetism is shown by lanthanoid ions. The paramagnetism arises due to the presence of unpaired electrons in f-orbital. Magnetic moment depends upon orbital and spin magnetic moment together. Neodymium shows maximum paramagnetism.

(vi) **Colour** Most of the trivalent ions are coloured in solid as well as in aqueous solution both due to partly filled f-orbital.

(vii) **Complex formation** Lanthanoids have low density due to large size and high charge. As a result, they have poor tendency to form complex.

(viii) **Ionisation enthalpy** The first ionisation enthalpies of lanthanoids are around 600 kJ mol^{-1}, the second about1200 kJmol^{-1} comparable with those of calcium. The variation of the third ionisation enthalpies indicates that the exchange enthalpy consideration (as in $3d$-orbital of 1st transition series) appears to impart a certain degree of stability to empty, half-filled and completely filled *f*-orbitals as indicated by the abnormally low third ionisation enthalpies of La, Gd, Lu.

(ix) **Chemical behaviour** The first few members of the series are quite reactive, almost like calcium. However, with increasing atomic number, their behaviour becomes similar to that of aluminium. These combine with hydrogen, carbon, nitrogen sulphides and halides. They also form oxides (M_2O_3 type) and hydroxides[$M(OH)_3$ type], which are basic like alkaline earth metal oxides and hydroxides.



Chemical reactions of the lanthanoids

Uses

(i) Lanthanoids are used for the production of alloy steels for plates and pipes.

(ii) Mischmetal alloy of lanthanoid is used in Mg-based alloy to produce bullets, shell and lighter flint.

(iii) Mixed oxides of lanthanoids are used as catalyst in cracking of petroleum.

(iv) Some lanthanum oxides are used as phosphorus in television screens.

ACTINOIDS

These are the elements in which last electron filled in $5f$-orbitals. The actinoids are radioactive elements and the earlier members possess relatively long half-lives while the latter ones have half-life values ranging from a day to 3 min. for lawrencium ($Z = 103$). The latter members could be prepared only in nanogram quantities.

Properties of Actinoids

Some properties of actinoids are discussed below:

(i) **Electronic configuration** The general electronic configuration is $5f^{1-14}6d^{0-1}7s^2$. The irregularities in the electronic configuration of actinoids is due to the stabilities of f^0, f^7 and f^{14} occupancies of $5f$-orbitals.

Electronic Configuration of Actinoids

Atomic number	Name	Symbol	Outer electronic structure
89	Actinium	Ac	$6d^17s^2$
90	Thorium	Th	$6d^27s^2$
91	Protactinium	Pa	$5f^26d^17s^2$
92	Uranium	U	$5f^36d^17s^2$
93	Neptunium	Np	$5f^46d^17s^2$
94	Plutonium	Pu	$5f^67s^2$
95	Americium	Am	$5f^77s^2$
96	Curium	Cm	$5f^76d^17s^2$
97	Berkelium	Bk	$5f^97s^2$
98	Californium	Cf	$5f^{10}7s^2$
99	Einsteinium	Es	$5f^{11}7s^2$
100	Fermium	Fm	$5f^{12}7s^2$
101	Mendelevium	Md	$5f^{13}7s^2$
102	Nobelium	No	$5f^{14}7s^2$
103	Lawrencium	Lr	$5f^{14}6d^17s^2$

(ii) **Ionic size** The radii of trivalent and quadrivalent ions of actinoids contract slightly with increasing atomic number due to **actinoid contraction**. This contraction results from poor shielding experienced by $5f$-electrons.

(iii) **Oxidation states** Actinoids show a variety of oxidation states due to comparable energies of $5f$, $6d$ and $7s$ energy levels. The dominant oxidation state of actinoids is + 3 which show increasing stability for the heavier elements.

(iv) **Magnetic properties** Actinoids are strongly paramagnetic. Their magnetic moments are smaller than the theoretically predicted values as the $5f$-electrons of actinoids are less effectively shielded which results in quenching of orbital combination.

(v) **Colour of the ions** Actinoid ions are generally coloured due to f-f transition. It depends upon the number of unpaired electrons in $5f$-orbitals.

(vi) **Complex formation** Actinoids have greater tendency to form complexes due to higher nuclear charge and smaller size of their atoms.

Similarities between Lanthanoids and Actinoids

There are some similarities between lanthanoids and actinoids, which are

(i) Both exhibit + 3 oxidation state predominantly.
(ii) Both are electropositive and have high reactivity.
(iii) Like lanthanoid contraction, there is actinoid contraction also.
(iv) They show ion exchange behaviour.
(v) In both series, f-orbitals are being progressively filled.

Difference between lanthanoids and actinoids

Property	Lanthanoids	Actinoids
Oxidation states	They show mainly + 3 oxidation state. + 2 and + 4 oxidation states also exist.	In addition to + 3 oxidation state, actinoids also show higher oxidation states like + 4, + 5, + 6 and + 7.
Binding energies	Binding energies of 4*f* are higher.	Binding energies of 5*f* are lower.
Shielding effect	They have poor shielding effect.	They have even poor shielding effect than lanthanoids.
Magnetic properties	They are paramagnetic and their magnetic properties can be easily explained.	They are also paramagnetic, but their magnetic properties cannot be easily explained.
Chemical reactivity		
(i) Tendency to form complexes	Less	More
(ii) Radioactivity	Except promethium, these are non-radioactive substances.	These are radioactive substances.
(iii) Basic character	These are less basic.	These are more basic.

Applications of *f*-Block Elements

Some applications of f-block elements are:

(i) Lanthanoids are used as catalyst in petroleum cracking.
(ii) Lanthanoids are used in producing alloys.
(iii) Oxides of lanthanoids are used to produce red colour on television screen.
(iv) Actinoids are used in nuclear reactors for the production of electricity.
(v) Actinoids are also used for the synthesis of transuranic elements.

TOPIC PRACTICE 3

OBJECTIVE Type Questions

1. Outermost electronic configuration of lanthanide is
(a) $4f^{1-14}, 5d^0, 6s^2$
(b) $4f^{1-14}, 5d^{0-1}, 6s^2$
(c) $4f^{0-14}, 5d^{0-2}, 6s^2$
(d) $4f^{0-14}, 5d^1, 6s^2$

2. Which of the following elements shows maximum number of different oxidation states in its compounds?
(a) Eu (b) La (c) Gd (d) Am

3. As the atomic number of lanthanides increases, there atomic radius decreases, but exception is
(a) Ga and Eu
(b) Eu and Yb
(c) Nd and Ho
(d) Dy and Ho

4. Which of the following has abnormally low value of third ionisation enthalpy. **NCERT Exemplar**
(a) Lanthanum
(b) Gadolinium
(c) Lutetium
(d) All of these

5. Which of the following oxidation state is common for all lanthanoids? **NCERT Exemplar**
(a) +2
(b) +3
(c) +4
(d) +5

6. Choose the appropriate option about the misch metal.
(a) It is an alloy which consists of a lanthanoid metal (~95%) and iron (~5%) and traces of S, C, Ca and Al
(b) Used in Mg based alloy to produce bullets, shell and lighter flint
(c) It finds application in making aeroplane body
(d) Both (a) and (b)

7. There are 14 elements in actinoid series. Which of the following elements does not belong to this series? **NCERT Exemplar**
(a) U (b) Np (c) Tm (d) Fm

VERY SHORT ANSWER Type Questions

8. Write down the electronic configuration of gadolinium (Gd). Its atomic number is 64.

9. What are the different oxidation states exhibited by lanthanoids? **NCERT**

10. Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state. **Delhi 2014**

11. Name the elements which are used for the synthesis of transuranic elements.

12. What are the uses of mischmetal?

SHORT ANSWER Type I Questions

13. Name the members of the lanthanoid series which exhibit + 4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configuration of these elements. **NCERT**

14. Actinoid contraction is greater from element to element than lanthanoid contraction. Why? **NCERT Intext**

15. Although, Zr belongs to 4*d* and Hf belongs to 5*d* transition series but it is quite difficult to separate them, why? **NCERT Exemplar**

16. Use Hund's rule to derive the electronic configuration of Ce^{3+} ion and calculate its magnetic moment on the basis of 'spin only' formula. **NCERT**

17. Write down the electronic configuration of the following and predict their magnetic moments.
(i) Ce^{4+} (ii) Pm^{3+}
(iii) Lu^{2+} (iv) Th^{4+}

18. The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements. **NCERT**

19. What are inner-transition elements? Decide which of the following atomic numbers are of the inner-transition elements 29, 59, 74, 95, 102, 104? **NCERT**

SHORT ANSWER Type II Questions

20. Compare the chemistry of actinoids with that of the lanthanoids with reference to
(i) electronic configuration
(ii) oxidation state
(iii) chemical reactivity **NCERT**

21. What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses. **NCERT**

22. The outer electronic configurations of two members of the lanthanoid series are as follows : $4f^1 5d^1$ and $4f^7 5d^0 6s^2$.

What are their atomic numbers? Predict the oxidation states exhibited by these elements in their compounds.

23. Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element. **NCERT**

24. What is lanthanoid contraction? Name an important alloy which contains some of the lanthanoid metals. **All India 2013**

LONG ANSWER Type Questions

25. (i) Yb^{2+} acts as a reductant while Tb^{4+} act as an oxidant. Why?

(ii) Account for the following.

(a) Paramagnetism is shown by lanthanoid ions. Comment.

(b) Compare the basic strength of $Ln(OH)_3$, $Ca(OH)_2$ and $Al(OH)_3$.

(c) Lanthanoids do not form their carbonyl compounds.

HINTS AND EXPLANATIONS

1. (*b*) Lanthanide exhibit $4f^{1-14}, 5d^{0-1}, 6s^2$ electronic configuration.

2. (*d*) Americium (Am) shows maximum number of different oxidation states in its compounds.

3. (*b*) In Eu and Yb, as atomic number increases atomic radius increases, which is an exception.

4. (*c*) La, Gd and Lu, all have abnormally low value of third ionisation enthalpy.

5. (*b*) Lanthanoids show common oxidation state of +3. Some of which also show +2 and +4 stable oxidation state alongwith +3 oxidation state. These are shown by those elements which by losing 2 or 4 electrons acquire a stable configuration of f^0, f^7 or f^{14}, e.g.

Eu^{2+} is $[Xe]4f^7$, Yb^{2+} is $[Xe]4f^{14}$, Ce^{4+} is $[Xe]4f^0$ and Tb^{4+} is $[Xe]4f^7$.

6. (*c*) Misch metal is an alloy which consists of a lanthanoid metal (~95%) and iron (~5%) and traces of S, C, Ca and Al. It is used in Mg based alloy to produce bullets, shell and lighter-flint.

7. (*c*) Tm ($Z = 69$) do not belong to actinoid series. The actinoid series is with atomic numbers 90 to 103. Thulium (Tm) has atomic number 69 belongs to lanthanoids ($4f$ series).

8. The electronic configuration of gadolinium is

$${}_{64}Gd = {}_{54}[Xe]4f^7 5d^1 6s^2$$

It has extra stability due to half-filled $4f$-subshell.

9. + 2, + 3 and + 4 (most common is + 3).

10. Cerium (Ce) is well known to exhibit +4 oxidation state.

11. Uranium

12. Bullets, shells, lighter flint are prepared by this alloy.

13. Refer to text on page 158.

14. The decrease in atomic (or ionic) radii (actinoid contraction) in actinoids is greater than lanthanoid contraction because $5f$-electrons have poor shielding effect as compared to $4f$-electrons. Therefore, the effect of increased nuclear charge leading to contraction in size, is more in case of actinoids.

15. Refer to text on pages 158 and 159.

16. Ce ($Z = 58$) = $[Xe]4f^1 5d^1 6s^2$

$Ce^{3+} = {}_{54}[Xe]4f^1$ (only one unpaired electron),

i.e. $n = 1$

According to 'spin-only' formula,

Magnetic moment of Ce^{3+} $(\mu) = \sqrt{n(n+2)}$ BM

$= \sqrt{1(1+2)}$ BM $= \sqrt{3}$ BM $= 1.73$ BM

17. Refer to text on pages 158 and 160.

18. Lanthanoids show limited number of oxidation states as +2, +3 and +4 (out of which +3 is most common). This is due to the large energy gap between $4f$ and $5d$-subshells. The dominant oxidation state of actinoids is also +3 but they show a number of other oxidation states also like uranium ($Z = 92$) and plutonium ($Z = 94$) show +3, +4, +5 and +6, neptunium ($Z = 93$) shows +3, + 4 +5 and +7. This is due to small energy difference between $5f$, $6d$ and $7s$-subshells of actinoids.

19. **Inner-transition elements** Refer to text on page 158. Inner-transition elements include lanthanoids (58-71) and actinoids (90-103). Thus, elements with atomic numbers 59, 95 and 102 are inner-transition elements.

20. Refer to text on pages 158 and 160.

21. An alloy is a homogeneous mixture of two or more metals or non-metals. It is prepared by blending the metals (and/ or non-metal) in molten state.

Refer to text on page 159.

22. Refer to text on pages 158 and 159.

23. Refer to text on page 160.

24. Refer to text on pages 158 and 159.

25. (i) **Hint** $Yb = 4f^{14}5s^2$, $Yb^{2+} = 4f^{14}5s^0$

$Tb = 4f^9 5s^2$, $Tb^{4+} = 4f^7 5s^0$

(ii) (a) Refer to text on page 159.

(b) Refer to text on page 158.

(c) Refer to text on page 159.

SUMMARY

d-block elements (or transition elements)

- The element lying between s-and f-block elements of the periodic table are collectively known as transition elements. Their general configuration $(n-1)d^{1-10}$, ns^{1-2}.
- Almost all d-block elements have electronic structure that features an outer pair of s-electrons, within which there is a partially or half or fully filled d-subshell.
- Generally the atomic radii of d-block elements in a series decrease with increase in atomic numbers but the decrease in atomic size is small after midway.
- Due to increase in nuclear charge which accompanies the filling of the inner d-orbitals there is an increase in ionisation enthalpy along each series of the transition element from left to right.
- They show variable oxidation state because the energy level of 3d, 4d and 5d orbitals are fairly close to those of 4s, 5s and 6s respectively.
- Most of transition elements and their compounds show paramagnetism and formed coloured compounds. The paramagnetism first increases in any transition element series and then decreases.
- Transition metals and their ions show strong tendency for complex formation.
- Small non-metallic atoms such as H, B, C and N are able to occupy interstitial space of the lattice of the d-block elements to form combinations which are termed as interstitial compounds.
- Transition metals and their compounds have catalytic properties, form a large number of alloys.
- Some of the important compounds of d-block elements are $K_2Cr_2O_7$ and $KMnO_4$.

f-block elements or inner transition elements

- The most characteristic oxidation state of lanthanides is +3
- The lanthanide contraction refers to ionic radius of that series. The separation of lanthanides is done by the ion exchange method which is based on size of hydrate M^{3+} ions.
- All the lanthanide ions with the exception of Lu^{3+}, Yb^{3+} and Ce^{4+} are paramagnetic because they contains unpaired electron in the 4f-orbitals.
- Magnetic moments of lanthanides are calculated by taking into consideration spin as well as orbital contributions.
- The covalent character of hydroxides of lanthanides increases and basicity of decreases as the size decreases from La^{3+} to Lu^{3+}.
- The elements with atomic number 90 to 103 are called actinides. These elements involve the filling of 5f-orbitals.
- The dominant oxidation state of actinides are generally coloured which is due to f-f transitions. It depends on the number of electrons in 5f-orbitals.
- Like lanthanides, actinides are strongly paramagnetic.
- Magnetic moments of actinides are less than the theoretically predicted value. This is due to the fact that 5f-electrons of actinides are less effectively shielded.
- Actinides have greater tendency to form complexes because of higher nuclear charge and smaller size of their atoms.
- There is a regular decrease in ionic and atomic radii with increase in the atomic number from Th to Lr. This is called actinide contraction. This is due to imperfect shielding of one 5d-electron by another in the same shell.

CHAPTER PRACTICE

OBJECTIVE Type Questions

1 Which of the following element show catalytic property?
(a) Ca (b) Fe
(c) Pb (d) None of these

2 Transition elements have unique property that
(a) they show variable oxidation state
(b) these elements acts as catalyst
(c) they form coloured compounds
(d) All of the above

3 Across the lanthanide series, the basicity of the lanthanide hydroxides
(a) increases
(b) decreases
(c) first increases and then decreases
(d) first decreases and then increases

4 The incorrect statement about cerium is
(a) its common oxidation states are +3 and +4
(b) +3 state is more stable than +4
(c) +4 state is not seen in solution
(d) Ce (IV) is an oxidant

CASE BASED Questions

Case I

Transition metals show a great variety of oxidation states in its compounds (variable valency) except the first and the last element. This is because of the fact that, the difference in the energy of $(n-1)$ d-electrons and ns-electrons is low which implies that electrons from both energy levels can take part in bonding.

In $3d$-series, all elements show $+2$ oxidation state except Sc ($Sc = +3$). Oxidation states first increases from Sc to Mn due to increase in number of unpaired electrons and then decreases because pairing takes place. Fe and Ni show zero oxidation state in metal carbonyls.

The oxidation state of a metal in a solvent depends on the nature of the solvent, e.g. Cu^+ is unstable in aqueous solution and undergo disproportionation reaction.

Low oxidation states are found if a complex compound has ligands capable of π-acceptor character and σ-bonding, e.g. $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero in the presence of CO as ligand.

The following questions are multiple choice questions. Choose the most appropriate answer :

5 Transition elements show oxidation states of
(a) +2 (b) +5
(c) 0 (d) variable

6 The highest oxidation state of a metal exhibited in its
(a) oxide
(b) fluoride
(c) sulphide
(d) both (a) and (b)

Or Name the oxometal anion of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.
(a) $[V_2O_5]^{2-}$ (b) $[MnO_7]^{2-}$
(c) $[MnO_4]^{2-}$ (d) $[V_2O_5]^-$

7 Name the element showing maximum number of oxidation states among the first series of transition metals from Sc to Zn.
(a) Mn (b) Sc
(c) V (d) Cr

8 Name the element which shows only +3 oxidation state.
(a) Mn (b) Sc
(c) V (d) Cr

Case II

Within the $3d$ series, manganese exhibits oxidation states in aqueous solution from +2 to +7, ranging from $Mn^{2+}(aq)$ to $MnO_4^-(aq)$. Likewise, iron forms both $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ as well as the FeO_4^{2-} ion. Cr and Mn form oxyions CrO_4^{2-}, MnO_4^-, owing to their willingness to form multiple bonds.

The pattern with the early transition metals. d and f in the $3d$ series up to Mn, and for the $4d$, $5d$ metals up to Ru and Os is that the maximum oxidation state corresponds to the number of "outer shell" electrons.

The highest oxidation states of $3d$ metals may depend upon the complex formation (e.g. the stabilisation of Co^{3+} by ammonia) or upon the pH (thus $MnO_4^{2-}(aq)$ is prone to disproportionation in acidic solution).

Within the 3d series, there is considerable variation in relative stability of oxidation states, sometimes on moving from one metal to a neighbour; thus, for iron, Fe^{3+} is more stable than Fe^{2+}, especially in alkaline conditions, while the reverse is true for cobalt. The ability of transition metals to exhibit a wide range of oxidation states is marked with metals such as vanadium, where the standard potentials can be rather small, making a switch between states relatively easy.

In the following questions, a statement of assertion followed by a statement of reason is given.

Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement. **CBSE Question Bank**

9 **Assertion** Highest oxidation state is exhibited by transition metal lying in the middle of the series.

Reason The highest oxidation state exhibited corresponds to number of $(n-1)d$ electrons.

10 **Assertion** Fe^{3+} is more stable than Fe^{2+}.

Reason Fe^{3+} has $3d^5$ configuration while Fe^{2+} has $3d^6$ configuration.

11 **Assertion** Vanadium had the ability to exhibit a wide range of oxidation states.

Reason The standard potential of vanadium are rather small, making a switch between oxidation states relatively easy.

12 **Assertion** Transition metals like Fe, Cr and Mn form oxyions.

Reason Oxygen is highly electronegative and has a tendency to form multiple bonds.

13 **Assertion** The highest oxidation states of the 3d metals depends only on electronic configuration of the metal.

Reason The number of electrons in the $(n-1)d$ and ns subshells determine the oxidation states exhibited by the metal.

ASSERTION and REASON

■ **Directions** (Q. Nos. 14-18) *In the following questions. an Assertion (A) is followed by a corresponding Reason (R) Use the following keys to choose the appropriate answer.*

(a) Both (A) and (R) are correct, (R) is the correct explanation of (A).

(b) Both (A) and (R) are correct, (R) is not the correct explanation of (A).

(c) (A) is correct; (R) is incorrect.

(d) (A) is incorrect; (R) is correct.

14 **Assertion** (A) Cr^{2+} is reducing, while Mn^{3+} is oxidising even both have d^4-configuration.

Reason (R) Configuration of Cu changes from d^3 to d^4.

15 **Assertion** (A) $KMnO_4$ oxidises oxalic acid to CO_2 and itself changes to Mn^{2+} ion.

Reason (R) $KMnO_4$ acts as an oxidising agent.

16 **Assertion** (A) Many trivalent lanthanoid ions are coloured both in solid state and in aqueous solution.

Reason (R) Colour of these ions is due to the presence of f-electrons.

17 **Assertion** (A) The highest oxidation state of osmium is +8.

Reason (R) Osmium is a 5d-series element.

18 **Assertion** (A) Transition metals are good catalysts.

Reason (R) V_2O_5 or Pt is used in the preparation of H_2SO_4 by contact process.

VERY SHORT ANSWER Type Questions

19 Why does the transition element scandium (Z = 21) not exhibit variable oxidation states?

20 Explain the large difference in melting point of Cr (1920°C) and Zn (420°C).

21 Calculate the 'spin only' magnetic moment of $M^{2+}(aq)$ ion. (Z = 27).

22 Why does copper metal not replace hydrogen from acid?

23 Why are the E° values of Mn, Zn more negative than expected?

24 The atomic size of Fe, Co and Ni are nearly same. Explain with reason.

25 Why Zn^{2+} salts are white while Ni^{2+} salts are blue?

26 Out of $[Sc(H_2O)_6]^{3+}$ and $[Ti(H_2O)_6]^{3+}$ ions, which is coloured and why? Give reason.

27 What factors led to the appearance of colour in the transition elements?

28 In chromic acid, (CrO_3), Cr has d^0 configuration but it is bright orange coloured solid, why?

29 Draw the structures of manganate ion and permanganate ion.

30 Write the formula of compound in which transition metal is in +6 oxidation state.

SHORT ANSWER Type I Questions

31 Reactivity of transition elements decreases almost regularly from Sc to Cu. Why?

32 Why there is striking similarities (horizontal and vertical) among successive members of the transition series?

33 Chromium is a typical hard metal while mercury is a liquid. Why?

34 What happens when
(i) $KMnO_4$ is heated? (ii) $K_2Cr_2O_7$ is heated?

35 Why fluorine is stabilises in low oxidation states of transition metals?

36 Complete the following equations.
(i) $2MnO_4^- + 5S^{2-} + 16H^+ \longrightarrow$
(ii) $Cr_2O_7^{2-} + 2OH^- \longrightarrow$

37 Write the oxidation reaction of iodide to iodate ion by potassium permanganate.

38 Explain why $Cr_2O_7^{2-}$ ion is a powerful oxidant in acidic medium but weak oxidant in basic medium?

39 (i) In the titration of Fe^{2+} ions with $KMnO_4$ in acidic medium, dil. H_2SO_4 is used but not the dil. HCl. Why?
(ii) Arrange the following oxides of Mn in the order of their decreasing acidic nature.
$MnO, Mn_2O_3, Mn_3O_4, MnO_2, Mn_2O_7$.

40 (i) Why Cu^+ salts are colourless, while Cu^{2+} salts are coloured?
(ii) The elements of *d*-series exhibit a larger number of oxidation states than the elements of *f*-series. Explain.

41 What happens when
(i) H_2S reacts with acidified $K_2Cr_2O_7$ solution?
(ii) ethanol is oxidised with acidified $K_2Cr_2O_7$ solution?

SHORT ANSWER Type II Questions

42 How would you account for the following?
(i) Copper (I) is diamagnetic, whereas copper (II) is paramagnetic.
(ii) What is the common oxidation state of Cu, Ag, Au?
(iii) The d^1-configuration is very unstable in ions.

43 Give examples and suggest reasons for the following features of the transition metal chemistry.
(i) The lowest oxide of transition metal is basic; the highest is amphoteric/acidic.
(ii) A transition metal exhibits highest oxidation state in oxides and fluorides.
(iii) The highest oxidation state is exhibited in oxoanions of a metal

44 Explain the following:
(i) The paramagnetic character in 3*d* transition series increases upto Cr and then decreases.
(ii) Transition metals are very good catalyst.
(iii) Transition metals form a large number of interstitial compounds.

45 Chromium is used extensively in steel alloys. It is extracted from its ore chromite ($FeCr_2O_4$), which contains chromium in +3 oxidation state.
(i) Give the electronic configuration of the elements iron and chromium.
(ii) What is the oxidation state of iron in chromite?

46 The $E°$ value in respect of electrodes of chromium ($Z = 24$), manganese ($Z = 25$) and iron ($Z = 26$) are
$Cr^{3+} / Cr^{2+} = -0.4$ V; $Mn^{3+} / Mn^{2+} = 1.5$ V
$Fe^{3+} / Fe^{2+} = +0.8$ V
On the basis of the above information, compare the feasibilities of further oxidation of their +2 oxidation state.

47 Write the chemical equations for the following reactions:
(i) Oxidation of nitrite ion by MnO_4^- in acidic medium.
(ii) Acidification of potassium chromate solution.
(iii) Disproportionation of Mn(VI) in acidic solution.

48 Although Cu^+ does not exist in solution state, but CuCl (s) is formed in the presence of Cl^- ions in aqueous solution of Cu(*s*) and Cu^{2+}. Explain.

49 Which oxoanion (among VO_4^{3-}, CrO_4^{2-}, MnO_4^{2-} or FeO_4^{2-}) is strongest oxidant and which is weak oxidant?

50 (i) How $KMnO_4$ can be obtained from MnO_2, KOH and KNO_3?
(ii) K_2PtCl_6 is a well known compound whereas corresponding Ni compound is not known. State the reason for it.

51 Describe the factors on which the stability of an oxidation state of lanthanoid elements depends.

52 The first few members of the series are quite reactive. They usually form oxides and hydroxides. Complete the following reactions of lanthanoids.
(i) $Ln \xrightarrow{\text{Heated with N}}$ (ii) $Ln \xrightarrow{\text{With halogens}}$
(iii) $Ln \xrightarrow{\text{Burns in } O_2}$

53 (i) NbF_4 is paramagnetic while NbX_4 (X = Cl, Br, I) are diamagnetic, why?
(ii) Out of $La(OH)_3$ and $Lu(OH)_3$, which is more basic and why?

54 Write the chemical equations for the following reactions :

(i) Disproportionation of Mn^{3+} in acidic medium.

(ii) Disproportionation of MnO_4^{2-} in alkaline medium.

(iii) Disproportionation of MnO_4^{2-} in acidic medium.

55 Complete the following reactions:

(i) $MnO_4^-(aq) + S_2O_3^{2-}(aq) + H_2O\ (l) \longrightarrow$

(ii) $Cr_2O_7^{2-}(aq) + H_2S\ (g) + H^+(aq) \longrightarrow$

(iii) $MnO_4^-(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$.

LONG ANSWER Type Questions

56 (i) Write the steps involved in the preparation of (a) $K_2Cr_2O_7$ from Na_2CrO_4. (b) $KMnO_4$ from K_2MnO_4.

(ii) What is the effect of lanthanoid contraction on the chemistry of the lanthanoids?

57 (i) A blackish brown coloured solid *A* which is an oxide of manganese, when fused with alkali metal hydroxide and an oxidising agent like KNO_3, produces a dark green coloured compound *B* which on disproportionation in neutral and acidic solution gives a purple coloured compound *C*.

Identify *A*, *B* and *C* and write the reaction involved when compound *C* is heated to 513 K.

(ii) (a) $E^\circ_{M^{3+}/M^{2+}}$ values for the first series of transition elements are given below:

E°(V)	Ti	V	Cr	Mn	Fe	Co
M^{3+}/M^{2+}	−0.37	−0.26	−0.41	+1.57	+0.77	+1.97

Identify the two strongest oxidising agents in the aqueous solution from the above data.

(b) Copper (I) ion is not known in aqueous solution. Explain.

(c) In this series the highest oxidation state of a metal is exhibited in its oxide. Identify the metal.

58 (i) Distinguish the structure of chromate ion from that of dichromate ion.

(ii) Between the dichromates of sodium and potassium, which one is preferred for oxidising organic compound and why?

(iii) Give two equations that explains the nature of $K_2Cr_2O_7$ as reducing agent.

ANSWERS

1. (b) **2.** (d) **3.** (b) **4.** (c)

5 (*d*) This is because of the fact that the difference in the energy of $(n-1)\,d$ electrons and *ns*-electrons is low which implies that electrons from both energy levels can take part in bonding.

6 (*d*) Oxygen and fluorine both have small size and high value of electronegativity. So, they can oxidise the metal to their highest oxidation states.

Or (*c*) $[MnO_4]^-$. Here, group number of equals to oxidation number of manganese, i.e. 7.

7 (*a*) Manganese. **8** (*b*) Scandium.

9 (*c*) Higher oxidation state is exhibited by manganese which is a transition metal lying in the middle of the series. Manganese exhibits oxidation states in aqueous solution from + 2 to +7. The highest oxidation state corresponds to the number of outershell electrons.

10 (*a*) Fe^{+3} is more stable than Fe^{+2} because Fe^{+3} has $3d^6$ configuration while, Fe^{+2} has $3d^5$ i.e. half-filled, stable configuration.

11 (*a*) Vanadium had the ability to exhibit a wide range of oxidation states from +2 to +5. The standard potentials of vanadium are rather small due to stability of V^{2+} as it has a half-filled t_{2g} level.

12 (*b*) Transition metals like Fe, Cr and Mn form oxyions (i.e. $\rightarrow MnO_4^-, FeO_4^{2-}, CrO_4^{2-}$) oxygen is highly electronegative and has a tendency to from multiple bonds because it has 6 valence electrons.

13 (*d*) The highest oxidation states of the 3*d* metals depends mainly less energy gap between 3*d* and 4*s*. It has maximum number of electrons to lose or share (as all the 3*d* electrons are unpaired). The number of electrons in the $(n-1)d$ and *ns* subshells determine the oxidation states exhibited by the metal.

14 (*c*) Cr^{2+} is reducing, while Mn^{3+} is oxidising when both have d^4 configuration. Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half-filled t_{2g} level. On the contrary, the change from Mn^{3+} to Mn^{2+} results in the half-filled (d^5) configuration which has extra stability. Thus, (A) is correct but (R) is incorrect.

15 (*a*) $KMnO_4$ oxidises oxalic acid to CO_2 and itself changes to Mn^{2+} ion, which is colourless, because $KMnO_4$ acts as an oxidising agent.

Both (A) and (R) are correct and (R) is the correct explanation of (A).

16 (*a*) Many trivalent lanthanoid ions are coloured due to the presence of unpaired *f*-electrons in solid state as well as in aqueous solutions. Both (A) and (R) are correct and (R) is the correct explanation of (A).

17 (*b*) Both (A) and (R) are correct but R is not the correct explanation of (A). The highest oxidation state of osmium is +8 due to its ability to expand their octet by using its all 8 electrons (2 from 6*s* and 6 from 5*d*).

18 (*b*) Due to larger surface area and variable valenices, transition metals form intermediate adsorbed complex easily, hence they are used as good catalysts. Thus, both (A) and (R) are correct but (R) is not the correct explanation of (A).

19 Electronic configuration of Sc = $3d^1 4s^2$. Hence, it shows +3 as the only oxidation state.

20 **Hint** Cr : $3d^5 4s^2$, Zn : $3d^{10} 4s^2$

21 Magnetic moment $\mu = \sqrt{n(n+2)}$ BM

Electronic configuration of $M = [Ar]3d^7 4s^2$

$M^{2+} = [Ar]3d^7 4s^0$

$\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

so, $\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.89$ BM

22 As copper is less reactive than hydrogen.

23 Negative E^{-} values of Mn^{2+} and Zn^{2+} are related to stabilities of half filed and completely filled configuration respectively.

24 **Hint** Addition of electrons in the d-subshell increases the screening effect.

25 Electronic configuration of $Zn^{2+} = 3d^{10}4s^0$

$= \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$

Electronic configuration of $Ni^{2+} = 3d^8 4s^0$

$= \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

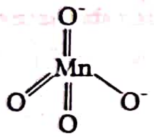
Compounds that contains unpaired electrons are coloured.

26 **Hint** Compounds that contains unpaired electrons are coloured.

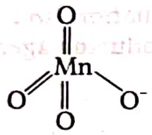
27 **Hint** (i) $d-d$ transitions, (ii) Charge transfer.

28 Due to charge transfer.

29



Manganate



Permanganate ion

30 K_2MnO_4

31 Refer to text on page 142.

32 This is because of the fact that along a horizontal row, electrons enters an incomplete inner shell while outer shell remains unchanged. In vertical coloumns, similarities are due to similar electronic configurations.

33 Cr have $3d^5 4s^1$. Hence metallic bonds are very strong.

34 (i) Refer to text on page 153. (ii) K_2CrO_4, Cr_2O_3, O_2

35 **Hint** Fluorine can form only single bonds.

36 (i) Refer to text on page 154.
(ii) Refer to text on page 152.

37 Refer to text on page 154.

38 Refer to text on page 152.

39 (i) $KMnO_4$ in presence of dil. H_2SO_4 acts as oxidising agent and oxygen produced oxidises ferrous salt to ferric salt.

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MinSO_4 + 5Fe(SO_4)_3 + 8H_2O$$

$KMnO_4$ is presence of dil. HCl also acts as oxidising agent but oxygen produced is used up partly for oxidation of HCl.

$$2KMnO_4 + 4HCl \longrightarrow 2KCl + 2MnCl_2 + 2H_2O + 6[O]$$

$$2HCl + [O] \longrightarrow H_2O + Cl_2$$

(ii) $Mn_2O_7 > MnO_2 > Mn_2O_3 > Mn_3O_4 > MnO$

40 (i) **Hint** $Cu^+ = 3d^{10}$ and $Cu^{2+} = 3d^9$.
(ii) Refer to text on pages 143 and 160.

41 (i) Refer to text on page 152.
(ii) $CH_3CH_2OH + K_2Cr_2O_7 \xrightarrow{\Delta} CH_3COOH$ (acidified)

42 (i) **Hint** $Cu^+ = 3d^{10}$ and $Cu^{2+} = 3d^9$
(ii) Common oxidation state of Cu, Ag and Au is +1.
(iii) As after loosing 1 more electron it will become stable. All elements with d^1 configuration are either reducing agent or undergo disproportionation.

43 (i) Refer to text on page 151 and 152.
(ii) Refer to text on page 142.
(iii) Refer to text on page 142.

44 (i) Refer to text on page 143. (ii) Refer to text on page 144.
(iii) Refer to text on page 143.

45 (i) Refer to text on page 138.
(ii) **Hint** Oxidation state of Fe=+2

46 **Hint** Order of stability of +2 oxidation state
$= Cr^{2+} < Fe^{2+} < Mn^{2+}$

47 (i) Refer to text on page 154. (ii) Refer to text on page 152.
(iii) Refer to text on page 153.

48 Refer to text on page 142.

49 Strongest oxidant = MnO_4^{2-}, weakest oxidant $= VO_4^{3-}$

50 (i) Refer to text on page 153.
(ii) This is because Pt^{4+} is more stable then Ni^{4+} as the sum of four ionisation enthalpies of Pt is use than of Ni.

51 Refer to text on page 159.

52 Refer to text on page 159.

53 (i) **Hint** Using Fajan's rule
(ii) **Hint** Size of lanthanoid ions decreases from La^{3+} to Lu^{3+}.

54 (i) Refer to text on page 153. (ii) Refer to text on page 153.
(iii) Refer to text on page 153.

55 (i) Refer to text on page 154. (ii) Refer to text on page 152.
(iii) Refer to text on page 153.

56 (i) (a) Refer to text on page 152.
(b) Refer to text on page 153.
(ii) Refer to text on page 158.

57 (i) **Hint** $A = MnO_2$ (pyrolusite) $B = K_2MnO_4$ $C = KMnO_4$
(ii) (a) Ti and V (b) Refer to text on page 142.
(c) Manganese

58 (i) Refer to text on page 152.
(ii) **Hint** Potassium
(iii) Refer to text on page 152.

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05

COORDINATION COMPOUNDS

Certain elements, that include mostly transition metals, have exceptional ability to bond with other charged or neutral atoms or molecules to form addition compounds through coordination bonds. The complex structure, thus formed, is known as coordination complex or coordination compound. Due to their unusual structure, hence the exceptional properties, coordination compounds play prominent roles both in natural and industrial processes, which make the study of these compounds, an important and challenging area of modern inorganic chemistry.

CHAPTER CHECKLIST

- Coordination Compounds: Nomenclature and Isomerism
- Bonding and Magnetic Behaviour
- Metal Carbonyls, Stability and Significance of Coordination Compounds

|TOPIC 1|

Coordination Compounds : Nomenclature and Isomerism

ADDITION COMPOUNDS

When two or more stable compounds combine together in stoichiometric ratio, then the compound formed is called addition compound. On the basis of how the addition compounds dissociate, these are classified into two main types, namely, coordination compounds and double salts.

Coordination Compounds

Addition compounds which exhibit properties completely different from their constituents and retain their identity even in solution state are called coordination compounds.

e.g. Potassium hexacyanoferrate (II), ($K_4[Fe(CN)_6]$), when dissolved in water gives K^+ and $[Fe(CN)_6]^{4-}$ ions in the solution. This solution does not show any properties of Fe^{2+} or CN^- ions.

Note

Complex ions are the ions in which the central metal ion is bonded to one or more molecules or ions. The ion $[Fe(CN)_6]^{4-}$ is a complex ion. They are also known as coordination complexes because they are Lewis acid-base complexes. The salt of the complex ions are called complex compounds or coordination compounds.

Double Salts

These are the addition compounds which are stable in the solid state but break up into constituents in dissolved state. These compounds show some properties of their constituent ions too. It contains two salts in equimolar ratio which are crystallised together and form their saturated solution.

e.g. Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, when dissolved in water gives Fe^{2+}, NH_4^+ and SO_4^{2-} ions and shows the properties of these ions during their respective tests.

Difference between double salts and coordination compounds

Double salts	Coordination compounds
They lose their identity in solution.	They don't completely lose their identity in solution.
They exist only in solid state and dissociate into ions in aqueous solution or in other solvent.	They exist in solid state as well as ions when dissolved in water or any other solvent. They don't dissociate into simple ions completely.
Their properties are essentially the same as those of its constituent compounds.	Their properties are different from their constituents.
In a double salt, metal ions exhibit their normal valency.	In a complex compound or coordination compound, metal ion satisfies two types of valencies called primary and secondary valencies.
e.g. Mohr's salt $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$, potash alum $[K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O]$, etc.	e.g. $[Ni(NH_3)_6]Cl_2$, $K_4[Fe(CN)_6]$, etc.

WERNER'S THEORY OF COORDINATION COMPOUNDS

Alfred Werner (1866-1919), a Swiss chemist was the first to formulate his ideas about the structures of coordination compounds in 1898. He proposed the concept of a **primary valence** and a **secondary valence** for a metal ion. Binary compounds such as $CrCl_3$, $CoCl_2$ and $PdCl_2$ have primary valence of 3, 2 and 2 respectively. In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess $AgNO_3$ solution in cold but some remained in the solution.

(i) 1 mole of $CoCl_3 \cdot 6NH_3$ (yellow) gave 3 moles of AgCl.
(ii) 1 mole of $CoCl_3 \cdot 5NH_3$ (purple) gave 2 moles of AgCl.
(iii) 1 mole of $CoCl_3 \cdot 4NH_3$ (green) gave 1 mole of AgCl.
(iv) 1 mole of $CoCl_3 \cdot 4NH_3$ (violet) gave 1 mole of AgCl.

On the basis of results of conductivity measurement in solution, above observations can be explained, if

(i) six groups in all either Cl^- ions or NH_3 molecules or both remain bonded to cobalt ion during reaction.
(ii) the compounds are formulated to form a single entity which does not dissociate in the reaction condition as

Formulation of cobalt (III) chloride-ammonia complexes

Colour	Formula	Solution conductivity corresponds to
Yellow	$[Co(NH_3)_6]^{3+}\ 3Cl^-$	1 : 3 electrolyte
Purple	$[CoCl(NH_3)_5]^{2+}\ 2Cl^-$	1 : 2 electrolyte
Green	$[CoCl_2(NH_3)_4]^+\ Cl^-$	1 : 1 electrolyte
Violet	$[CoCl_2(NH_3)_4]^+\ Cl^-$	1 : 1 electrolyte

Note that last two compounds in the above table have identical empirical formula, $CoCl_3 \cdot 4NH_3$ but have distinct properties. Such compounds are termed as **isomers**.

Werner called secondary valence for the number of groups bounded directly to the metal ion. In each of the above complexes secondary valencies are six.

Postulates of Werner's Theory

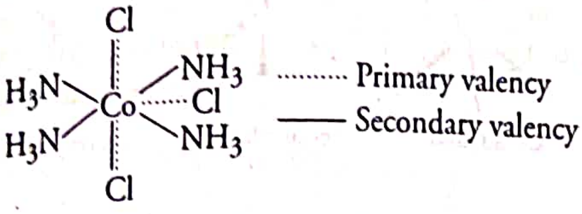
(i) In coordination compounds, metal has two types of linkages (valencies)-primary and secondary in a complex.

(ii) Primary valency is equal to the oxidation number of central ion. It is non-directional and ionisable. It is satisfied by **negative** ions, e.g. in $CrCl_3$, the primary valency is three.

(iii) Secondary valency is equal to the coordination number of central atom/ion. It is directional and non-ionisable. It is commonly satisfied by neutral molecules or negative ions and is always fixed for a metal. Each metal ion has a fixed number of secondary valency. e.g. In $[Co(NH_3)_6]Cl_3$, three Cl^- ions are held by primary valency and six NH_3 groups are held by secondary valency. They are directed in space and account for shape or structure of a complex ion, e.g. $[Co(NH_3)_6]^{3+}$ has octahedral shape.

(iv) The ions or groups bounded by the secondary linkages to the metal have characteristic spatial arrangements called coordination polyhedra.

e.g. Structure of $[CoCl_2(NH_3)_4]^+Cl^-$ is as follows:



The solid and dotted lines together indicate Cl-atom satisfying both primary and secondary valency.

(v) Werner further postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals thus, $[Co(NH_3)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$ and $[CoCl_2(NH_3)_4]^+$ are octahedral entities, while $[Ni(CO)_4]$ and $[PtCl_4]^{2-}$ are tetrahedral and square planar, respectively.

DEFINITIONS OF SOME IMPORTANT TERMS USED IN COORDINATION COMPOUNDS

Coordination Entity

Coordination entity constitutes a central metal atom or ion attached to a fixed number of ions or molecules. It may be positive, negative or neutral. e.g. $[CoCl_3(NH_3)_3]$ is a coordination entity in which cobalt ion is surrounded by three NH_3 molecules and three Cl^- ions. Other examples are $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$, $[Ni(CO)_4]$ and $[PtCl_2(NH_3)_2]$.

Central Metal Atom or Ion

In a coordination entity, the metal atom or ion to which a fixed number of ions/groups are bounded in a definite geometrical arrangements around it, is called central metal atom or ions.

e.g. In $[NiCl_2(H_2O)_4]$, $[CoCl(NH_3)_5]^{2+}$ and $[Fe(CN)_6]^{3-}$, Ni^{2+}, Co^{3+} and Fe^{3+} respectively are central metal or ions which are also called Lewis acids.

Ligands

Molecules or ions which donate a lone pair of electron to the central atom or ion are called ligands. These are the ions or molecules bound to the central atom/ion through coordinate bond in the coordination entity. It is a Lewis base. These may be simple ions such as Cl^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ or even molecules, such as proteins.

Ligands are classified into three categories on the basis of charge:

(i) **Neutral ligands** $H_2\ddot{\underset{..}{O}}$, CO, $\ddot{N}H_3$, NO, etc.

(ii) **Negative ligands** F^-, Cl^-, Br^-, I^-, OH^-, CN^-, SO_4^{2-}, etc.

(iii) **Positive ligands** NO^+, NO_2^+, $NH_2—NH_3^+$, etc.

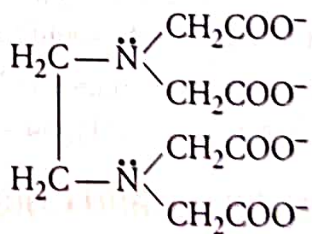
On the basis of denticity (donor sites/number of ligating groups), ligands are classified as follows:

(i) **Unidentate** When a ligand is bonded through one donor site to central metal atom/ion, it is said to be unidentate ligand, e.g. Cl^-, CO, NH_3, H_2O, etc.

(ii) **Didentate or bidentate** When a ligand is bonded through two donor sites to central metal atom/ion, it is said to be didentate ligand, e.g. 1, 2-ethanediamine $(NH_2—CH_2—CH_2—NH_2)$ or $C_2O_4^{2-}$ (oxalate), etc.

(iii) **Polydentate** The ligands which contains three or more donor atoms, are called polydentate ligands, e.g. ethylenediaminetetraacetate ion ($EDTA^{4-}$). It is an important hexadentate ligand.

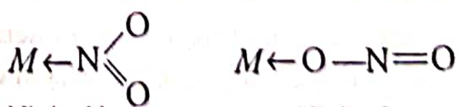
It can bind through two nitrogen and four oxygen atom to a central metal ion.



(iv) **Ambidentate ligands** When a ligand is bonded through two different atoms, it is said to be ambidentate ligand, e.g. NO_2^-, SCN^-, CN^-

NO_2^- ion can coordinate either through nitrogen or oxygen to central metal ion.

Similarly, SCN^- ion can coordinate through sulphur or nitrogen atom.



Nitrito-N Nitrito-O

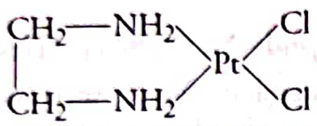
$M \leftarrow SCN$ $M \leftarrow NCS$

Thiocyanato Isothiocyanato

(v) **Chelating ligands** When a di- or polydentate ligand uses its two or more donor sites to bind a single metal ion, it is called a chelating ligand. The number of such ligating groups is called the **denticity** of the ligand.

The chelating ligands form more stable complexes than the unidentate analogs because when chelation occurs, entropy decreases and the process becomes more favourable and forms a ring complex which is known as chelate ligand or chelating ring.

e.g.



Structure of $[Pt(en)Cl_2]$

Coordination Number (CN)

The total number of ligand donor atoms, attached directly to the metal ion in a complex is called coordination number.

e.g. $[Co(NH_3)_6]^{3+}$, CN of Co = 6

$[Ni(CO)_4]$, CN of Ni = 4

$[Co(en)_3]^{3+}$, CN of Co $= 3 \times 2 = 6$ ($\because$ en is didentate)

$[Fe(C_2O_4)_3]^{3+}$, CN of Fe $= 3 \times 2 = 6$

($\because C_2O_4^{2-}$ is didentate)

$[PtCl_6]^{2-}$, CN of Pt = 6

$[Ni(NH_3)_4]^{2+}$, CN of Ni = 4

π(pi) bonds, if formed between the ligand and the central atom/ion, are not counted for the coordination number.

The coordination number is determined only by the number of sigma (σ) bonds formed by the ligand with atom/ion.

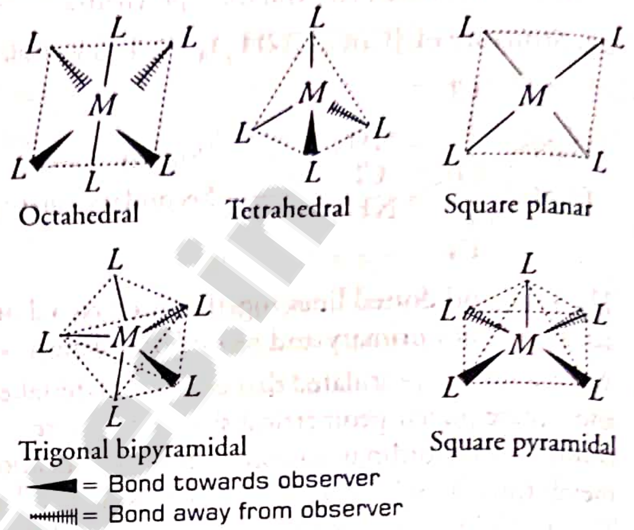
Coordination Sphere and Counter Ions

The central atom/ion and the ligands attached to it are enclosed in the square bracket and are collectively known as coordination sphere. The ionisable groups are written outside the bracket and are known as counter ions or ionisation sphere, e.g. in $K_4[Fe(CN)_6]$, the coordination sphere is $[Fe(CN)_6]^{4-}$ and the counter ion is $4K^+$.

Coordination Polyhedron

It is the spatial arrangement of the ligand atoms which are directly attached to the central atom/ion. The most common coordination polyhedra are octahedral, square planar and tetrahedral.

e.g. $[Co(NH_3)_6]^{3+}$ is octahedral, $[Ni(CO)_4]$ is tetrahedral and $[PtCl_4]^{2-}$ is square planar.



Shapes of different coordination polyhedra, where, *M* is central atom/ ion and *L* is a unidentate ligand

Charge on the Complex Ion

The charge carried by a complex ion is the algebraic sum of the charges carried by the central metal ion and the total ligands attached to the central metal ion. e.g. In the complex ion, $[Ag(CN)_2]^-$, Ag^+ ion carries a charge of +1 and each CN^- ion carries a charge of –1. Therefore, the net charge on complex ion $[Ag(CN)_2]^-$ is one negative $(+1-2=-1)$.

Oxidation Number of Central Atom

Oxidation number of central atom in a complex is defined as the charge it would carry when all the ligands are removed along with electron pairs which are shared with central atom. The oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity.

e.g. In $[Cu(CN)_4]^{3-}$, oxidation number of Cu is +1 and it is written as Cu(I). Oxidation number of central atom is a charge on central atom.

Homoleptic and Heteroleptic Complexes

Complexes in which a metal is bound to only one kind of donor groups, e.g. $[Co(NH_3)_6]^{3+}$ are known as **homoleptic complexes**. Complexes in which a metal is bound to more than one kind of donor groups, e.g. $[Co(NH_3)_4Cl_2]^+$ are known as **heteroleptic complexes**.

NOMENCLATURE OF COORDINATION COMPOUNDS

The formula and names adopted for the coordination entities are based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC). The rules for the nomenclature of coordination compounds are as follows:

1. Formulae of Mononuclear Coordination Entities

The formula of a compound is a shorthand tool used to provide basic information about the constitution of the compound in a concise and convenient manner. Mononuclear coordination entities contain a single central metal atom.

Following rules are applied while writing the formulae:

(i) The central atom is listed first.

(ii) The ligands are then listed in alphabetical order. The placement of a ligand, in the list does not depend on its charge.

(iii) Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.

(iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulae are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.

(v) There should be no space between the ligands and the metal within a coordination sphere.

(vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. e.g. $[Co(CN)_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, etc.

(vii) The charge of the cation(s) is balanced by the charge of the anion(s).

Note IUPAC, in 2004, recommends that ligands will be sorted alphabetically. Charge has no role in it.

2. Naming of Mononuclear Coordination Compounds

The names of coordination compounds are derived by following the principles of additive nomenclature, i.e. the groups that surround the central atom must be identified in the name. They are listed as prefixes to the name of the central atom along with any appropriate multipliers.

The following rules are used while naming coordination compounds:

(i) The cation is named first in both positively and negatively charged coordination entities.

(ii) The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula).

(iii) Names of the anionic ligands end in -'o', those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. These are placed within enclosing marks ( ).

(iv) Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, *bis, tris, tetrakis* are used, the ligand to which they refer is placed in parenthesis. e.g.$[NiCl_2(PPh_3)_2]$ is named as dichloro*bis*- (triphenylphosphine)nickel(II).

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

(vi) If the complex ion is a cation, the metal is named same as the element, e.g. Co in a complex cation is called cobalt and Pt is called platinum.
If the complex ion is an anion, the name of the metal ends with the suffix—'ate', e.g. Co in a complex anion, $[Co(SCN)_4]^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions, e.g. ferrate for Fe.

(vii) The neutral complex molecule is named similar to that of the complex cation. e.g.

- $[Pt(NH_3)_2Cl(NO_2)]$ is named as Diamminechloridonitrito-N-platinum(II)
- $K_3[Cr(C_2O_4)_3]$ is named as Potassium trioxalatochromate(III)
- $[CoCl_2(en)_2]Cl$ is named as Dichlorido*bis*-(ethane-1,2-diamine)cobalt (III) chloride
- $[Cr(NH_3)_3(H_2O)_3]Cl_3$ is named as Triamminetriaquachromium(III) chloride
- $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$ is named as *tris*-(ethane-1,2-diamine) cobalt(III) sulphate

EXAMPLE |1| Write down the IUPAC names of the following coordination compounds.

(i) $[Co(NH_3)_5Cl]Cl_2$,

(ii) $K_2[PdCl_4]$ **NCERT Intext**

Sol. (i) $[Co(NH_3)_5Cl]Cl_2$

$$x + (0) \times 5 + (-1) \times 1 + (-1) \times 2 = 0$$
$$x + 0 - 3 = 0$$
$$x = +3$$

So, the name of the complex is pentaamminechloridocobalt (III) chloride.

(ii) $K_2[PdCl_4]$

Counter ion ↑ Metal atom ↑ Ligand ↑ Ligand number ↑

Let the oxidation state of Pd is x.

$$(+1)2 + x + (-1)4 = 0$$
$$2 + x - 4 = 0$$
$$\Rightarrow \quad x = +2$$

So, the name of the complex is potassiumtetrchloridopalladate (II).

EXAMPLE |2| Write the formulae for the following coordination compounds.

(i) Tetraamminediaquacobalt(III) chloride

(ii) Potassium tetracyanonickelate(II)

(iii) *Tris* (ethane-1, 2-diamine) chromium(III) chloride

(iv) Amminebromidochloridonitrito-N-platinate(II)

(v) Dichlorido *bis*-(ethane-1, 2-diamine) platinum(IV) nitrate

(vi) Iron(III) hexacyanoferrate(II) **NCERT Intext**

Sol. (i) $\underbrace{\text{Tetraamminediaqua}}_{\text{Ligand}}\ \underbrace{\text{cobalt (III)}}_{\text{Metal}}\ \underbrace{\text{chloride}}_{\text{Counter ion}}$

$\overset{III}{[Co(NH_3)_4(H_2O)_2]}Cl_x$

To find the value of x, we have to find the charge on the complex.

$$\overset{III}{[Co(NH_3)_4(H_2O)_2]^+}$$

$$\Rightarrow \quad +3 + 4 \times 0 + 2 \times 0 = x$$
$$x = +3$$

So, the formula of the complex is $[Co(NH_3)_4(H_2O)_2]Cl_3$.

(ii) $\underbrace{\text{Potassium}}_{\text{Counter ion}}\ \underbrace{\text{tetracyano}}_{\text{Ligand}}\ \underbrace{\text{nickelate (II)}}_{\text{Metal}}\ K_x[\overset{II}{Ni}(CN)_4]$

To find the value of x, find the charge on the complex.

$[Ni(CN)_4]^{x-}$ (as K^+ is positive)

$$+2 + (-1) \times 4 = -x$$
$$-x = -2 \quad \text{or} \quad x = +2$$

So, the formula of the complex is $K_2[Ni(CN)_4]$.

Similarly,

(iii) $[Cr(en)_3]Cl_3$

(iv) $[Pt(NH_3)BrCl(NO_2)]^-$

(v) $[PtCl_2(en)_2](NO_3)_2$

(vi) $Fe_4[Fe(CN)_6]_3$

ISOMERISM IN COORDINATION COMPOUNDS

Two or more compounds having the same molecular formula but different arrangement of atoms are said to exhibit isomerism. They differ in one or more physical or chemical properties.

Two major types of isomerism are known among coordination compounds. These are as follows:

1. Structural Isomerism

The coordination compounds having same chemical formula but different structural arrangement are known as structural isomers. These isomers have different bonding pattern. It is further subdivided into following two types :

Linkage Isomerism

It is shown by the coordination compounds containing ambidentate ligand such as NO_2, SCN, etc. SCN can bind to metal through N and S as M—NCS and M—SCN, respectively. Similarly, NO_2 can bind either by N or by O of NO_2, e.g.

$$\underset{\text{Yellow}}{[Co(NH_3)_3(NO_2)]Cl_2} \text{ and } \underset{\text{Blue}}{[Co(NH_3)_3ONO]Cl_2}.$$

Coordination Isomerism

It arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex, e.g. $[Co(NH_3)_6][Cr(CN)_6]$ in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligand to Cr^{3+} and in its coordination isomer, $[Cr(NH_3)_6][Co(CN)_6]$, the NH_3 ligands are bound to Cr^{3+} and CN^- ligands to Co^{3+}. Similarly, $[Pt(NH_3)_4][PtCl_4]$ shows coordination isomerism.

Ionisation Isomerism

It arises when compounds give different ions in the solution although they have same composition. It arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion, e.g.

$$\underset{\text{(Red)}}{[Co(NH_3)_5SO_4]Br} \text{ and } \underset{\text{(Violet)}}{[Co(NH_3)_5Br]SO_4}.$$

Hydrate Isomerism or Solvate Isomerism

This type of isomerism arises in case where water is involved as a solvent. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice, e.g. aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (grey, green).

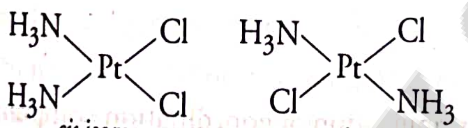
2. Stereoisomerism

Coordination compounds having same molecular as well as structural formulae but different arrangement in space in the polyhedral are called stereoisomers. This phenomenon is called stereoisomerism. It is further subdivided into two types:

Geometrical Isomerism

Heteroleptic complexes with coordination numbers 4 and 6 show this type of isomerism. It arises due to the difference in the geometrical arrangement of the ligands around the central metal ion. When same ligands occupy the adjacent position in the polyhedra, it is known as *cis*-isomer whereas when same ligands occupy the opposite position in the polyhedra, it is known as *trans*-isomer.

A square planar complex of the type $[MX_2L_2]$ (X and L are unidentate) shows these two geometrical isomers, e.g.



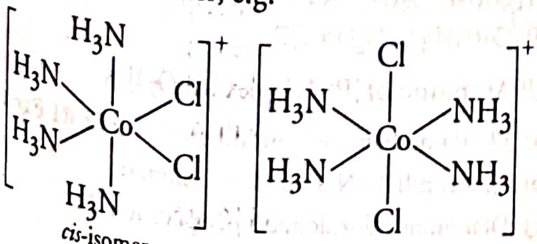
cis-isomer *trans*-isomer

Geometrical isomers of $[Pt(NH_3)_2Cl_2]$

Note

cis-isomer of $[Pt(NH_3)_2Cl_2]$ is also known as *cis*-platin which is used as an anticancer drug in the chemotherapy process of cancer treatment.

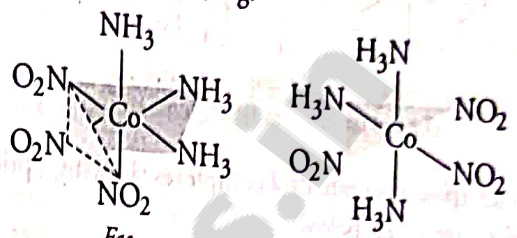
Other square planar complex of the type $[MABXL]$ ($ABXL$ are unidentate) shows three isomers-two *cis* and one *trans*. Such isomerism is not possible in a tetrahedral complexes but similar behaviour or isomerism is possible in octahedral complexes of the type $[MX_2L_4]$ in which two ligands X may be oriented *cis* or *trans* to each other, e.g.



cis-isomer *trans*-isomer

Geometrical isomers of $[Co(NH_3)_4Cl_2]^+$

Octahedral coordination entities of the type $[Ma_3b_3]$ shows geometrical isomerism. When three donor atoms of same ligands are occupying adjacent position in the polyhedra, it is known as facial (*fac*) isomer. Whereas when three same ligands are occupying position around the meridian of the octahedral, it is known as meridional (*mer*) isomer, e.g.



Fac *mer*

Facial *(fac)* and meridional *(mer)* isomers of $[Co(NH_3)_3(NO_2)_3]$

Hence, these isomers differ in one or more physical or chemical properties.

Note

Tetrahedral complex does not show geometrical isomerism because the relative positions of unidentate ligands attached to the central metal atom are the same with respect to each other.

Optical Isomerism

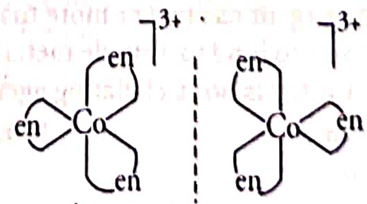
The compounds which do not have a plane of symmetry show optical isomerism. The optically active isomers have non-superimposable mirror images or which cannot be superimposed on one another and the molecules which cannot be superimposed are called **chiral**.

The two forms called *dextro* (d) or *laevo* (l), depending upon the direction they rotate the plane of polarised light in a polarimeter, are called **enantiomers.**

The isomer which rotate the plane of polarised light to the right is called *dextro* (d) rotatory whereas the isomer which rotate the plane of polarised light to the left is called *laevo* (l) rotatory.

An equimolar mixture of *dextro* (d) and *laevo* (l) rotatory isomers is called **racemic mixture.** Optical isomerism is commonly shown by the octahedral complexes involving didentate ligands.

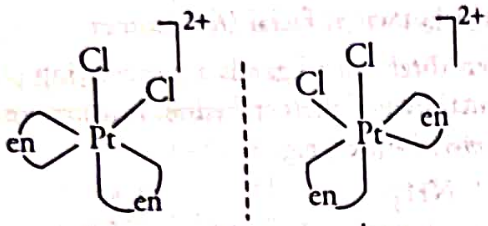
e.g. For $[Co(en)_3]^{3+}$ two isomers can be represented as :



dextro Mirror *laevo*

Optical isomers of $[Co(en)_3]^{3+}$

In a coordination entity of the type $[PtCl_2(en)_2]^{2+}$, only the *cis*-isomer shows optical activity.



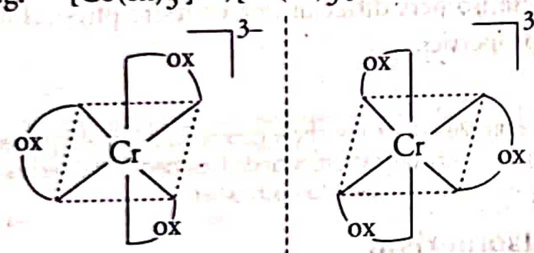
dextro Mirror *laevo*

Optical isomers of $[PtCl_2(en)_2]^{2+}$

Some examples of octahedral complexes showing optical isomerism are given below:

(i) Type $[M(AA)_3]$

e.g. $[Co(en)_3]^{3+}$, $[Cr(ox)_3]^{3-}$.

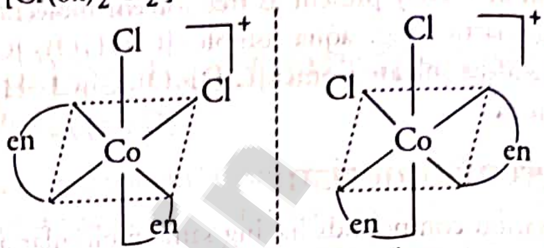


dextro Mirror *laevo*

Optical isomers of $[Cr(ox)_3]^{3-}$

(ii) Type $[M(AA)_2X_2]^{n+}$ or $[M(AA)_2XY]^{n+}$

e.g. *cis*-$[Co(en)_2Cl_2]^+$, *cis*-$[Pt(en)_2Cl_2]^+$, *cis*-$[Cr(ox)_2Cl_2]^{3-}$

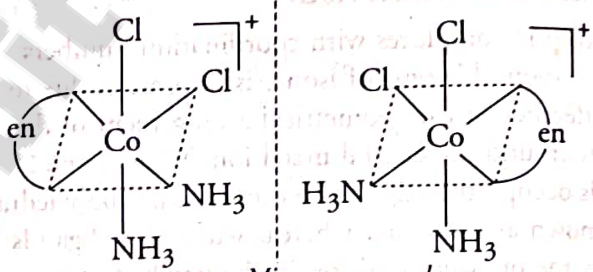


dextro Mirror *laevo*

Optical isomers of $[Co(en)_2Cl_2]$

(iii) Type $[M(AA)X_2Y_2]$

e.g. $[Co(en)(NH_3)_2Cl_2]^+$



dextro Mirror *laevo*

Optical isomers of $[Co(NH_3)_2(en)Cl_2]$

TOPIC PRACTICE 1

OBJECTIVE Type Questions

1. How many ions are produced from the complex $[Co(NH_3)_5Cl]Cl_2$ in solution? **All India 2020**

(a) 4 (b) 2
(c) 3 (d) 5

2. When 1 mole of $CrCl_3 \cdot 6H_2O$ is treated with excess of $AgNO_3$, 3 moles of AgCl are obtained. The formula of the complex is **NCERT Exemplar**

(a) $[CrCl_3(H_2O)_3] \cdot 3H_2O$
(b) $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$
(c) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$
(d) $[Cr(H_2O)_6]Cl_3$

3. A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent? **NCERT Exemplar**

(a) Thiosulphato
(b) Oxalato
(c) Glycinato
(d) Ethane-1, 2-diamine

4. The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species? **NCERT Exemplar**

(a) $[Fe(CO)_5]$
(b) $[Fe(CN)_6]^{3-}$
(c) $[Fe(C_2O_4)_3]^{3-}$
(d) $[Fe(H_2O)_6]^{3+}$

5. The formula of the coordination compound tetraammineaquachloridocobalt(III) chloride is **CBSE SQP 2021**

(a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$
(b) $[Co(NH_3)_4(H_2O)Cl]Cl_3$
(c) $[Co(NH_3)_2(H_2O)Cl]Cl_2$
(d) $[Co(NH_3)_4(H_2O)Cl]Cl$

6. IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$ is **NCERT Exemplar**

(a) Platinum diaminechloronitrite
(b) Chloronitrito-N-ammineplatinum (II)
(c) Diamminechloridonitrito-N-platinum (II)
(d) Diamminechloronitrito-N-platinate (II)

7. Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are **NCERT Exemplar**
(a) linkage isomers (b) coordination isomers
(c) ionisation isomers (d) geometrical isomers

8. The compounds $[Co(SO_4)(NH_3)_5]Br$ and $[Co(SO_4)(NH_3)_5]Cl$ represent **NCERT Exemplar**
(a) linkage isomerism (b) ionisation isomerism
(c) coordination isomerism (d) no isomerism

9. What kind of isomerism exists between $[Cr(H_2O)_6]Cl_3$ (violet) and $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (greyish-green)? **NCERT Exemplar**
(a) Linkage isomerism (b) Solvate isomerism
(c) Ionisation isomerism (d) Coordination isomerism

10. Indicate the complex ion which shows geometrical isomerism. **NCERT Exemplar**
(a) $[Cr(H_2O)_4Cl_2]^+$ (b) $[Pt(NH_3)_3Cl]$
(c) $[Co(NH_3)_6]^{3+}$ (d) $[Co(CN)_5(NC)]^{3-}$

VERY SHORT ANSWER Type Questions

11. How many ions are produced from the complex, $Co(NH_3)_6Cl_2$ in solution? **NCERT**

12. When a coordination compound $CrCl_3 \cdot 6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound, write structural formula of the complex. **All India 2019**

13. What is the difference between a complex and a double salt? **All India 2019**

14. Write the oxidation number of cobalt in $K[Co(CO)_4]$. **NCERT**

15. Write the coordination number and oxidation state of platinum in the complex $[Pt(en)_2Cl_2]$. **CBSE 2018**

16. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]Cl$. **Delhi 2014**

17. Write the IUPAC name of $K_3[Fe(C_2O_4)_3]$ **Delhi 2013 C**

18. Write the IUPAC name of the complex : $[CoCl_2(en)_2]^+$ **All India 2017**

19. How many geometrical isomers are possible in the following coordination entities?
(i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[Co(NH_3)_3Cl_3]$ **NCERT**

20. Why is geometrical isomerism not possible for tetrahedral complexes?

21. Why is optical isomerism not shown by square planar complexes?

22. What type of isomerism is exhibited by the complex $[Co(en)_3]^{3+}$? **Delhi 2014**

23. Which of the following is more stable complex and why?
$[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ **Delhi 2014**

SHORT ANSWER Type I Questions

24. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. Why? **NCERT**

25. Aqueous copper sulphate solution (blue in colour) gives
(i) a green precipitate with aqueous potassium fluoride.
(ii) a bright green solution with aqueous potassium chloride.
Explain these experimental results. **NCERT**

26. A coordination compound $CrCl_3 \cdot 4H_2O$ precipitates silver chloride when treated with silver nitrate. The molar conductance of its solution corresponds to a total of two ions. Write the structural formula of the compound and name it. **NCERT Exemplar**

27. Using IUPAC norms, write the formulae for the following :
(i) Sodium dicyanidoaurate (I).
(ii) Tetraamminechloridonitrito-N-platinum (IV) sulphate. **All India 2017**

28. Using IUPAC norms, write the formulae for the following:
(i) Potassium trioxalatoaluminate (III)
(ii) Dichlorido-bis-(ethane-1, 2-diamine) cobalt(III)

29. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S(g)$ is passed through this solution? **NCERT**

30. Name the type of isomerism when ambidentate ligands are attached to central metal ion. Give two examples of ambidentate ligands. **NCERT Exemplar**

31. Amongst the following, the most stable complex is
(i) $Fe(H_2O)_6]^{3+}$ (ii) $[Fe(NH_3)_6]^{3+}$
(iii) $[Fe(C_2O_4)_3]^{3-}$ (iv) $[FeCl_6]^{3-}$ **NCERT**

32. Using IUPAC norms, write the formulae for the following:
(i) Potassium tri(oxalato) chromate (III)
(ii) Hexaammine platinum (IV)
(iii) Tetrabromidocuprate (II)
(iv) Pentaamminenitrito-N-cobalt (III) **NCERT**

33. (i) Write the IUPAC name of the following complex.
$[Cr(NH_3)_2Cl_2(en)]Cl$ (en = ethylene diamine)
(ii) Write the formula for the following complex.
Pentaamminenitrito-O-cobalt (III) **Delhi 2015**

34. (i) Write the IUPAC name of the following complex.
$[Co(NH_3)_5Cl]^{2+}$
(ii) Write the formula for the following complex.
Potassium tetrachloridonickelate(II) **All India 2015**

35. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. What type of isomerism does it exhibit? **All India 2014**

36. Give the evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers. **NCERT Intext**

37. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers? **NCERT**

38. $CoSO_4Cl \cdot 5NH_3$ exists in two isomeric forms '*A*' and '*B*'. Isomer '*A*' reacts with $AgNO_3$ to give white precipitate, but does not react with $BaCl_2$. Isomer '*B*' gives white precipitate with $BaCl_2$ but does not react with $AgNO_3$.
Answer the following questions.
(i) Identify '*A*' and '*B*' and write their structural formulae.
(ii) Name the type of isomerism involved.
(iii) Give the IUPAC name of '*A*' and '*B*'. **NCERT Exemplar**

39. A complex of the type $[M(AA)_2X_2]^{n+}$ is known to be optically active. What does this indicate about the structure of the complex? Give one example of such complex. **NCERT Exemplar**

SHORT ANSWER Type II Questions

40. Explain the bonding in coordination compounds in terms of Werner's postulates. **NCERT**

41. Explain with two examples each of the following. Coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic. **NCERT**

42. What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each. **NCERT**

43. Specify the oxidation number of metal in the following coordination entities. **NCERT**
(i) $[Co(H_2O)(CN)(en)_2]^{2+}$ (ii) $[CoBr_2(en)_2]^+$
(iii) $[PtCl_4]^{2-}$

44. Using IUPAC norms, write the formulae for the following:
(i) Tetrahydroxozincate(II)
(ii) Potassium tetrachloridopalladate(II)
(iii) Diamminedichloridoplatinum(II)
(iv) Potassium tetracyanonickelate(II)
(v) Pentaamminenitrito-O-cobalt(III)
(vi) Hexaamminecobalt(III) sulphate **NCERT**

45. Using IUPAC norms, write the systematic names of the following:
(i) $[Ni(NH_3)_6]Cl_2$ (ii) $[Co(en)_3]^{3+}$
(iii) $[Ni(CO)_4]$ **NCERT**

46. Write the IUPAC name of the following coordination compounds.
(i) $[Cr(NH_3)_3Cl_3]$ (ii) $K_3[Fe(CN)_6]$
(iii) $[CoBr_2(en)_2]^+$
(en = ethylene diamine) **Delhi 2013**

47. Using IUPAC norms, write the systematic names of the following.
(i) $[Co(NH_3)_6]Cl_3$ (ii) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$
(iii) $[Ti(H_2O)_6]^{3+}$ **NCERT**

48. Using IUPAC norms, write the formulae for the following.
(i) Sodium hexafluoridosilicate (IV)
(ii) *Tri*-(ethane-1,2-diamine) chromium (III) chloride
(iii) Hexa-aquachromium (III) chloride

49. Draw the structures of optical isomers of
(i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[PtCl_2(en)_2]^{2+}$
(iii) $[Cr(NH_3)_2Cl_2(en)]^+$ **NCERT**

50. Draw all the isomers (geometrical and optical) of
(i) $[CoCl_2(en)_2]^+$ (ii) $[Co(NH_3)Cl(en)_2]^{2+}$
(iii) $[Co(NH_3)_2Cl_2(en)]^+$ **NCERT**

51. Write the types of isomerism exhibited by the following complexes.
(i) $[Co(NH_3)_5Cl]SO_4$ (ii) $[Co(en)_3]^{3+}$
(iii) $[Co(NH_3)_6][Cr(CN)_6]$ **Delhi 2013**

52. What type of isomerism is exhibited by $[Co(NH_3)_4Cl_2]^+Br^-$? Write the structures of the possible isomers and the state of hybridisation of the central metal atom. **Delhi 2013 C**

LONG ANSWER Type Questions

53. List various types of isomerism possible for coordination compounds, giving an example of each. **NCERT**

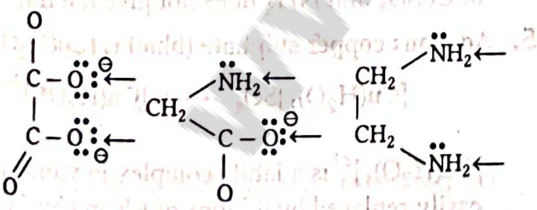
54. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers.
(i) $K[Cr(H_2O)_2(C_2O_4)_2]$
(ii) $[Co(en)_3]Cl_3$
(iii) $[Co(NH_3)_5(NO_2)](NO_3)_2$
(iv) $[Pt(NH_3)(H_2O)Cl_2]$ **NCERT Intext**

HINTS AND EXPLANATIONS

1. *(c)* Total three ions are produced from the complex $[Co(NH_3)_5Cl]Cl_2$ in solution. The ions are $[Co(NH_3)_5Cl]^{2+}$ and $2Cl^-$.

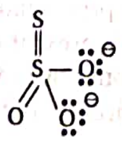
2. *(d)* 1 mole of $AgNO_3$ precipitates one free chloride ion (Cl^-). Here, 3 moles of AgCl are precipitated by excess of $AgNO_3$. Hence, there must be three free Cl^- ions.
So, the formula of the complex can be $[Cr(H_2O)_6]Cl_3$ and correct choice is (d).

3. *(a)* A chelating ligand has two or more binding donor atoms to a single metal ion.
e.g.



Oxalato Glycinato Ethane-1, 2 diamine

Here $(\leftarrow)$ denotes binding site.
Thiosulphato $(S_2O_3^{2-})$ is not a chelating ligand because geometrically it is not favourable for $S_2O_3^{2-}$ to chelate a metal ion.



4. *(c)* Chelation (formation of cycle by linkage between metal ion and ligand) stabilises the coordination compound.
The ligand which chelates the metal ion are known as chelating ligand.
Here, only $[Fe(C_2O_4)_3]^{3-}$ is a coordination compound which contains oxalate ion as a chelating ligand. Hence, it stabilises coordination compound by chelating Fe^{3+} ion.

5. *(a)* The formula of the coordination compound tetraammine aquachloridocobalt (III) chloride is $[Co(NH_3)_4(H_2O)Cl]Cl_2$ while writing the formulae, the central atom is listed first and the ligands are listed in alphabetical order.

6. *(c)* Correct IUPAC name can be written as
The ligands present in the given coordination compound are
(i) (NH_3) represented as amine
(ii) $Cl^{\ominus}$ represented as chlorido
(iii) $NO_2^{\ominus}$ represented as nitrito-N
According to IUPAC rule, ligands are named in an alphabetical order before central atom. Prefex di-will be used to indicate the number of NH_3 ligands present.
Oxidation state of metal is indicated by Roman numeral in parenthesis.
So, IUPAC name will be
diamminechloronitrito-N-platinum (II)
Hence, option (c) is correct.

7. *(a)* The ligand(s) which has two different bonding sites are known as ambident ligands e.g. NCS, NO_2 etc. Here, NCS has two binding sites at N and S. Hence, NCS (thiocyanate) can bind to the metal ion in two ways
$M \leftarrow NCS$ or $M \rightarrow SNC$

Thus, coordination compounds containing NCS as a ligand can show linkage isomerism, i.e. $[Pd(C_6H_5)_2(SCN)_2]$ and $[Pd(C_6H_5)_2(NCS)_2]$ are linkage isomers.
Hence, correct choice is (a).

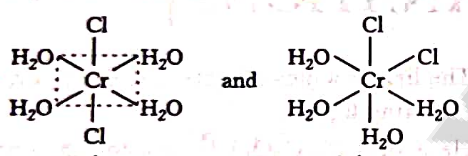
8. *(d)* Compounds having same molecular formula but different structural formula are known as isomers. $[Co(SO_4)_2(NH_3)_5]Br$ and $[Co(SO_4)(NH_3)_5]Cl$ have not same molecular formula. Hence, they are not isomers.

9. *(b)* Solvate isomerism is shown when two compounds having same molecular formula differ by whether a solvent molecule is directly bonded to metal ion or is present as free solvent molecules in the crystal lattice.

When water is present as solvent and show this type of isomerism then it is known as hydrate isomerism.

Coordination compound $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]H_2O\cdot Cl_2$ are solvate isomers, because water is exchanged by chloride ion. This is why both of them show different colour on exposure to sunlight.

10. *(a)* $[Cr(H_2O)_4Cl_2]^+$ shows geometrical isomerism because it is a MA_4B_2 type coordination compound which contains two set of equivalent ligands, four H_2O and 2 Cl. Hence, the possible geometrical isomers are



trans-isomer and *cis*-isomer

Hence, correct choice is (a).

11. The complex will dissociate in aqueous solution to produce three ions.

$Co(NH_3)_6Cl_2(aq) \longrightarrow [Co(NH_3)_6]^{2+} + 2Cl^-$

12. When one mole of $CrCl_3.6H_2O$ is mixed with $AgNO_3$, two moles of AgCl are precipitated which indicates that two ionisable chloride ions in the complex are present. Hence, its structural formula is $[CrCl(H_2O)_5]Cl_2.H_2O$.

13. Double salt is a combination of (+)ve and (–) ve ions, which completely dissociates into its ions, when dissolved in water. Whereas complex is a salt, in which molecular structure of complex ion retain itself in aqueous solution, i.e. donot dissociates into its ions completely.

14. $K[Co(CO)_4]$; $1 + x + 4 \times (0) = 0, \quad x = -1$

15. Coordination number of platinum in the complex, $[Pt(en)_2Cl_2]$ is 6 as *en* is a bidentate ligand. Let the oxidation state of Pt is x.

$\therefore \quad x + 0 + 2(-1) = 0$

$\Rightarrow \quad x = +2$

Thus, oxidation state of Pt is + 2.

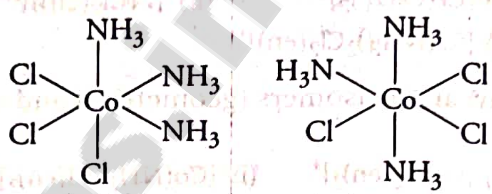
16. Tetraamminedichloridochromium(III) chloride.

17. Potassium trioxalatoferrate (III).

18. The IUPAC name of the complex $[CoCl_2(en)_2]^+$ is dichloridobis (ethane-1, 2- diamine) cobalt (III) ion.

19. (i) No geometrical isomer is possible.

(ii) Two geometrical isomers are possible for $[Co(NH_3)_3Cl_3]$.



Facial (*fac*) Meridional (*mer*)

20. Because relative positions of ligands attached to central metal atom are the same with respect to each other.

21. Because square planar complexes contain a plane of symmetry.

22. Complex $[Co(en)_3]^{+3}$ shows optical isomerism.

23. $[Co(en)_3]^{3+}$ is more stable complex because of chelation.

24. When $FeSO_4$ and $(NH_4)_2SO_4$ solutions are mixed in 1:1 molar ratio, Mohr's salt (a double salt) is formed.

$$FeSO_4(aq) + (NH_4)_2SO_4(aq) \longrightarrow FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$$

$$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \rightleftharpoons Fe^{2+}(aq) + 2NH_4^+(aq) + 2SO_4^{2-}(aq) + 6\,H_2O$$

Because Fe^{2+} ions are formed on dissolution of Mohr's salt, its aqueous solution gives the test of Fe^{2+} ions. But when $CuSO_4$ is mixed with ammonia, following reaction occurs :

$$CuSO_4(aq) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]SO_4$$

This complex does not produce Cu^{2+} ion, so the solution of $CuSO_4$ and NH_3 does not give the test of Cu^{2+} ion.

25. Aqueous copper sulphate (blue) is $[Cu(H_2O)_4]SO_4$.

$$[Cu(H_2O)_4]SO_4 \longrightarrow \underset{\text{Blue}}{[Cu(H_2O)_4]^{2+}} + SO_4^{2-}$$

$[Cu(H_2O)_4]^{2+}$ is a labile complex in which H_2O ligand get easily replaced by F^- ions of KF and by Cl^- ions of KCl.

(i) $[Cu(H_2O)_4]^{2+}(aq) + 4F^-(aq) \longrightarrow \underset{\text{Green ppt}}{[CuF_4]^{2-}} + 4H_2O$

(ii) $[Cu(H_2O)_4]^{2+}(aq) + 4Cl^-(aq) \longrightarrow \underset{\text{(Bright green ppt)}}{[CuCl_4]^{2-}} + 4\,H_2O$

26. Formation of white precipitate with $AgNO_3$ shows that atleast one Cl^- ion is present outside the coordination sphere. Moreover, only two ions are obtained in solution, so only one Cl^- is present outside the sphere.

Thus, the formula of the complex is $[Cr(H_2O)_4Cl_2]Cl$ and its IUPAC name is tetraaquadichloridocobalt (III) chloride.

27. (i) $Na[Au(CN)_2]$ - Sodium dicyanidoaurate (I)
(ii) $[Pt(NH_3)_4Cl(NO_2)]SO_4$-Tetraamminechlorido nitrito-N-platinum (IV) sulphate

28. (i) Potassium trioxalatoaluminate (III) $K_3[Al(C_2O_4)_3]$
(ii) Dichloridobis (ethane-1, 2-diamine) cobalt (III) $[CoCl_2(en)_2]^+$

29. When excess of KCN(*aq*) is mixed with $CuSO_4(aq)$, a complex named potassium tetracyanocuprate (II) is formed. Since, CN^- ions are strong ligands, the complex is quite stable. It is evident from the value of stability constant ($K = 2.0 \times 10^{27}$).

$$\underset{\text{(Excess)}}{5KCN(aq)} + CuSO_4(aq) \longrightarrow \underset{\underset{H_2S}{\downarrow}}{\underset{\text{(Soluble)}}{K_3[Cu(CN)_4](aq)}} + K_2SO_4(aq)$$

No cleavage and no production of Cu^{2+} ions.

30. Ligands having more than one different binding position are known as ambidentate ligands. e.g. SCN has two different binding positions S and N.
Coordination compounds containing ambidentate ligands are considered to show linkage isomerism due to the presence of two different binding positions.
e.g. (i) $[Co(NH_3)_5SCN]^{3+}$ and (ii) $[Fe(NH_3)_5(NO_2)]^{3+}$

31. In each complex, Fe is in + 3 state, as $C_2O_4^{2-}$ is didentate chelating ligand, which forms chelate rings and hence, it is the most stable complex.

32. (i) $K_3[Cr(C_2O_4)_3]$ (ii) $[Pt(NH_3)_6]^{4+}$
(iii) $[CuBr_4]^{2-}$ (iv) $[Co(NH_3)_5(NO_2)]^{2+}$

33. (i) $[Cr(NH_3)_2Cl_2(en)]Cl$ (en = ethylene diamine)
IUPAC name Diamminedichloridobis-(ethane-1, 2-diamine) chromium (III) chloride.
(ii) Pentaamminenitrito-o-cobalt (III)
Formula $[Co(NH_3)_5(ONO)]^{2+}$

34. (i) $[Co(NH_3)_5Cl]^{2+}$
IUPAC name Pentaamminechloridocobalt(III)
(ii) Potassium tetrachloridonickelate (II)
Formula $K_2[NiCl_4]$

35. $[Cr(NH_3)_4Cl_2]^+$
IUPAC name Tetraamminedichloridochromium (III) ion.
Isomerism It shows geometrical isomerism (*cis*-form and *trans*-form).

36. We dissolve both the compounds in water with different test tubes. To both the test tubes
Case I add $BaCl_2$ solution, one compound gives white ppt. indicating the presence of SO_4^{2-} ions.
The other compound does not give white precipitate, indicating the absence of SO_4^{2-} ions.

$$[Co(NH_3)_5Cl]SO_4 + BaCl_2(aq) \longrightarrow [Co(NH_3)_5Cl]Cl_2 + \underset{\text{White ppt.}}{BaSO_4(s)}$$

$$[Co(NH_3)_5SO_4]Cl + BaCl_2(aq) \longrightarrow \text{No reaction}$$

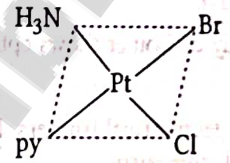
Case II add $AgNO_3$ solution to both the compounds in separate test tubes.
Only II compound gives white precipitate, not the I, due to the absence of Cl^- as counter ion.

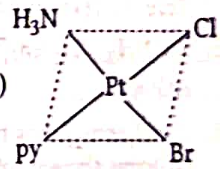
$$[Co(NH_3)_5SO_4]Cl + AgNO_3(aq) \longrightarrow [Co(NH_3)_5SO_4]NO_3 + \underset{\text{White ppt}}{AgCl(s)}$$

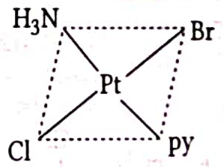
$$[Co(NH_3)_5Cl]SO_4 + AgNO_3(aq) \longrightarrow \text{No reaction}$$

These two test prove that the given two compounds are a pair of ionisation isomers.

37. There are three geometrical isomers of $[Pt(NH_3)Br(Cl)(py)]$ (These structures are obtained by fixing the position of one ligand, i.e. NH_3 and placing at the *trans*-position any one of the remaining three ligands one by one. Two of these are *cis* and one is *trans*).

(i)


(ii)


(iii)


Optical isomerism is not exhibited by the compound with CN= 4 and square planar geometry because of the presence of horizontal plane of symmetry.

38. '*A*' gives precipitate with $AgNO_3$, so in it Cl is present outside the coordination sphere.
'*B*' gives precipitate with $BaCl_2$, so in it SO_4^{2-} is present outside the coordination sphere.
(i) So, *A* - $[Co(NH_3)_5SO_4]Cl$ *B*- $[Co(NH_3)_5Cl]SO_4$
(ii) Ionisation isomerism (as give different ions when subjected to ionisation.)
(iii) [*A*], Pentaamminesulphatocobalt (III) chloride.
[*B*], Pentaamminechloridocobalt (III) sulphate.

39. An optically active complex of the type $[M(AA)_2X_2]^{n+}$ indicates *cis*-octahedral structure, e.g. *cis*- $[Pt(en)_2Cl_2]^{2+}$ or *cis*- $[Co(en)_2Cl_2]^+$ because its mirror image isomers is non-superimposable.
For the structure refer to text on page 176.

40. Refer to text on pages 170 and 171.

41. Refer to text on pages 171 and 172.

42. Refer to text on page 171.

43.

Coordination entities	Oxidation state
(i) $[Co(H_2O)(CN)(en)_2]^{2+}$	+3
(ii) $[CoBr_2(en)_2]^+$	+3
(iii) $[PtCl_4]^{2-}$	+2

44. (i) $[Zn(OH)_4]^{2-}$ (ii) $K_2[PdCl_4]$
(iii) $[Pt(NH_3)_2Cl_2]$ (iv) $K_2[Ni(CN)_4]$
(v) $[Co(NH_3)_5(ONO)]^{2+}$ (vi) $[Co(NH_3)_6]_2(SO_4)_3$

45. (i) Hexaamminenickel(II) chloride
(ii) *Tris*-(ethane-1,2-diamine)cobalt(III) ion
(iii) Tetracarbonylnickel (0)

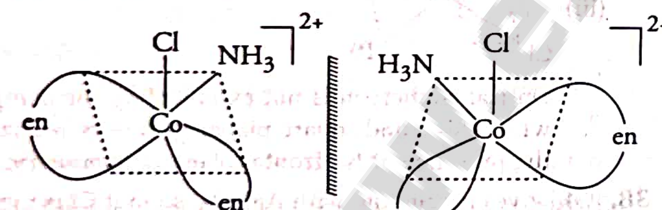
46. (i) Triamminetrichloridochromium(III)
(ii) Potassium hexacyanoferrate(III)
(iii) Dibromido*bis*-(ethane-1, 2-diamine) cobalt (III) ion

47. (i) Hexaamminecobalt(III) chloride
(ii) Diamminechlorido (methylamine) platinum(II) chloride
(iii) Hexaaquatitanium(III) ion

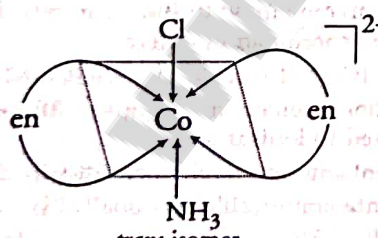
48. (i) $Na_2[SiF_6]$ (ii) $[Cr(en)_3]Cl_3$
(iii) $[Cr(H_2O)_6]Cl_3$
For rules refer to page 173.

49. (i) $[Cr(C_2O_4)_3]^{3-}$ Refer to text on page 176.
(ii) Refer to text on page 176.
(iii) $[Cr(NH_3)_2Cl_2(en)]^+$ (only *cis*-isomer shows optical activity)

50. (i) $[CoCl_2(en)_2]^+$ has two geometrical isomers. Further, *cis*-form shows optical isomerism.
Refer to text on page 176.
(ii) $[Co(NH_3)Cl(en)_2]^{2+}$



cis-isomer



trans-isomer

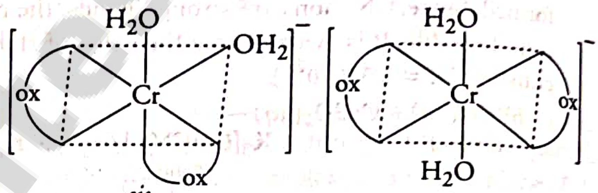
(iii) $[Co(NH_3)_2Cl_2(en)]^+$ Refer to text on page 176.

51. (i) $[Co(NH_3)_5Cl]SO_4$ shows ionisation isomerism.
$[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers.
(ii) $[Co(en)_3]^{3+}$ shows optical isomerism.
Refer to text on page 176.
(iii) Refer to text on page 174.

52. Ionisation isomerism and geometrical isomerism are exhibited by $[Co(NH_3)_4Cl_2]Br$. The ionisation isomers are $[Co(NH_3)_4Cl_2]Br$ and $[Co(NH_3)_4(Cl)(Br)]Cl$.
For structure, refer to text on page 175.
The central atom has d^2sp^3 hybridisation.

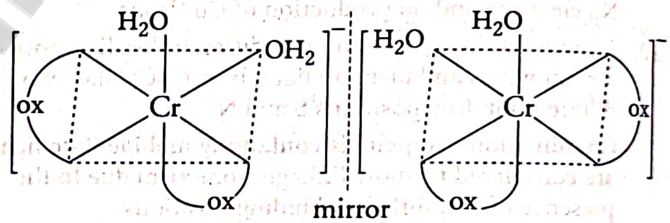
53. Refer to text on pages 174 and 175.

54. (i) It exists as both geometrical (*cis* and *trans*) and optical isomers.
(a) Geometrical isomers

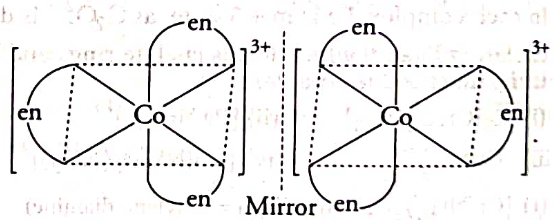


cis *trans*

(b) Optical isomers

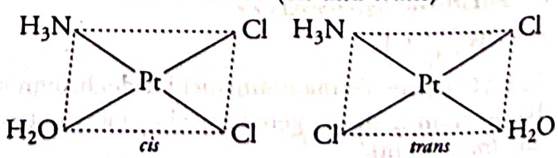


(ii) It shows two Optical isomers



(iii) **Ionisation isomers**
$[Co(NH_3)_5(NO_2)(NO_3)_2]$,
$[Co(NH_3)_5(NO_3)](NO_2)(NO_3)$
Linkage isomers
$[Co(NH_3)_5(NO_2)](NO_3)_2$,
$[Co(NH_3)_5(ONO)](NO_3)_2$

(iv) **Geometrical isomers** (*cis* and *trans*)



cis *trans*

|TOPIC 2|
Bonding and Magnetic Behaviour

BONDING IN COORDINATION COMPOUNDS

Werner was the first to explain the nature of bonding in coordination compounds but his theory was not able to answer the basic questions like :

(a) Why only some elements can form coordination compounds?

(b) Why the directional properties are exhibited by the bonds in coordination compounds?

(c) Why magnetic and optical properties are unique characteristic for coordination compounds?

Many approaches have been put forth to explain the nature of bonding in coordination compounds. These are Valence Bond Theory (VBT), Crystal Field Theory (CFT), Ligand Field Theory (LFT) and Molecular Orbital Theory (MOT).

VALENCE BOND THEORY

This theory was put forward by L. Pauling in 1930 to explain the shapes of the complexes.

The main points of this theory are as follows:

(i) Central atom/ion makes available required number of empty orbitals.

(ii) These orbitals undergo hybridisation by using $(n-1)d$, ns, np or ns, np, nd orbitals of central atom/ion under the influence of ligands to give same number of hybrid orbitals of equal energy and definite geometry, such as linear, tetrahedral, square planar and octahedral shapes as shown in the following table. These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

Hybridisation and geometry of complexes

Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

(iii) Ligands must have one sigma orbital containing lone pair of electrons.

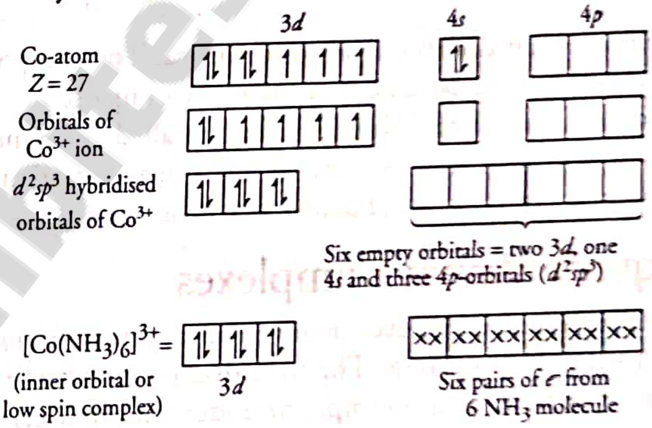
Octahedral Complexes

Octahedral complexes involve one s, three p and two d-orbitals. They can form inner orbital and outer orbital complexes.

Let us take some examples to explain octahedral complexes. These are as follows :

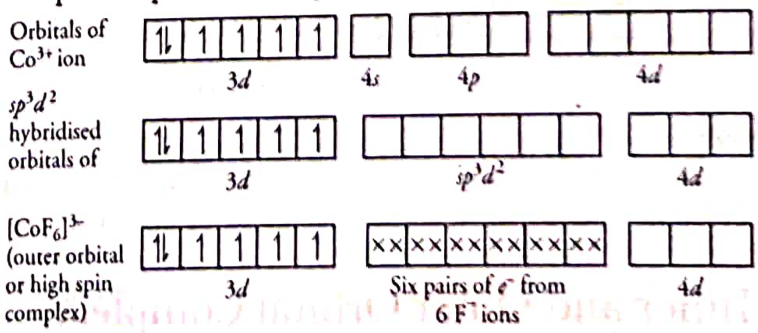
(i) $[Co(NH_3)_6]^{3+}$ In this complex, oxidation state of cobalt is +3 and electronic configuration of Co^{3+} ion is $[Ar]^{18}3d^6$.

Its hybridisation scheme can be shown as:



Six pairs of electrons one from each NH_3 molecule, occupy the six hybrid orbitals. Thus, complex has octahedral (d^2sp^3) geometry and is diamagnetic because of the absence of unpaired electrons.

(ii) $[CoF_6]^{3-}$ In $[CoF_6]^{3-}$, outer orbital $4d$ is used in hybridisation. Thus, it is called outer orbital or high spin or spin free complex.

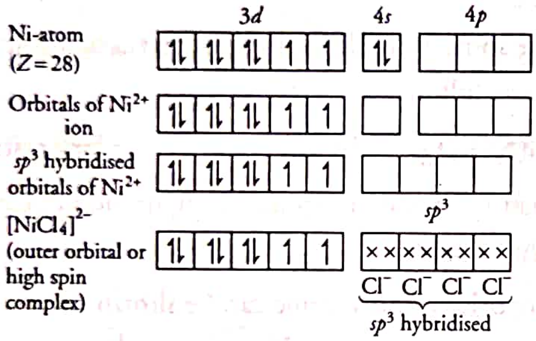


Six pairs of electrons one from each F^- ion occupy the six hybrid orbitals. Thus, the complex has octahedral geometry (sp^3d^2) and is paramagnetic because of the presence of four unpaired electrons.

Tetrahedral Complexes

In tetrahedral complexes, one *s* and three *p*-orbitals are hybridised to form four equivalent orbitals oriented tetrahedrally. Let us take an example to explain tetrahedral complexes.

$[NiCl_4]^{2-}$ In this complex ion, oxidation state of Ni is +2 and its valence shell configuration is $[Ar]^{18}3d^8$.



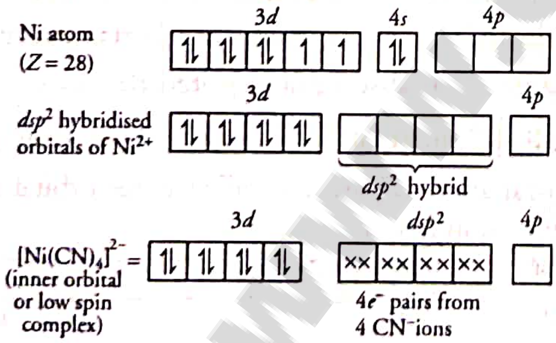
Each Cl^- ion donates a pair of electrons. The compound is paramagnetic, because it contains two unpaired electrons. Similarly, $[Ni(CO)_4]$ has tetrahedral geometry but it is diamagnetic because nickel is in zero oxidation state and contains no unpaired electrons.

Square Planar Complexes

Square planar complexes involve one *d*, one *s* and two *p*-orbitals for bonding. The hybridisation involved is dsp^2. Let us take an example to understand it clearly.

e.g. $[Ni(CN)_4]^{2-}$ has square planar shape.

Ni-atom (ground state) $=[Ar]3d^8, 4s^2, 4p^0$



Note

The hybrid orbitals do not actually exist. Infact, hybridisation is a mathematical manipulation of wave equation for the atomic orbitals involved.

Inner and Outer Orbital Complexes

When the complex formed involves the inner $(n-1)\,d$-orbitals for hybridisation, the complex is called inner orbital complex. The complex is diamagnetic because of the absence of unpaired electron. This type of complex is also called low spin or spin paired complex,

e.g. $[Ni(CN)_4]^{2-}$ and $[Co(NH_3)_6]^{3+}$ are inner orbital or **low spin or spin paired complex**, which are diamagnetic in nature. When the complex formed involves the outer *nd*-orbital for hybridisation, the complex is called outer orbital complex. The complex is paramagnetic because of the presence of unpaired electrons. This type of complex is also called **high spin or spin free complex.**

e.g. $[CoF_6]^{3-}$ and $[Ni(H_2O)_6]^{2+}$ are outer orbital or high spin or spin free complexes, which are paramagnetic in nature.

Magnetic Properties of Coordination Compounds

Magnetic nature of coordination compounds is due to the presence of unpaired electrons in molecules. These properties are very useful in understanding the structure and bonding in transition metal complexes. The magnetic moment of coordination compounds can be measured by the magnetic susceptibility experiments. The results can be used to obtain information about the structures of metal complexes.

Some complications revealed on the basis of critical study of magnetic data of coordination compounds are as follows:

(i) For metal ions upto three electrons in *d*-orbital (Ti^{3+}, V^{3+}, Cr^{3+}), two vacant *d*-orbitals are available for octahedral hybridisation using 4*s* and 4*p*-orbitals. The magnetic behaviour of these free ions and their coordination entities is similar.

(ii) When more than three $3d$ electrons are present, the required pair of $3d$ orbitals for octahedral hybridisation are not directly available because of Hund's rule, e.g. for d^4 (Cr^{2+}, Mn^{3+}), d^5 (Mn^{2+}, Fe^{3+}), d^6(Fe^{2+}, Co^{3+}) cases, a vacant pair of *d*-orbitals result only by pairing of $3d$ electrons which leaves two, one and zero unpaired electrons, respectively.

(iii) The magnetic data agree with maximum spin pairing in many cases especially with coordination compound containing d^6 ions. However, with species containing d^4 and d^5 ions there are complications.

Some examples are given below:

- $[Mn(CN)_6]^{3-}$ has magnetic moment of two unpaired electrons while $[MnCl_6]^{3-}$ has a paramagnetic moment of four unpaired electrons.
- $[Fe(CN)_6]^{3-}$ has paramagnetic moment of one unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons.

- $[CoF_6]^{3-}$ is paramagnetic due to the presence of four unpaired electrons while $[Co(C_2O_4)_3]^{3-}$ is diamagnetic. This is explained by VBT in terms of formation of inner orbital (d^2sp^3 hybridisation) and outer orbital (sp^3d^2 hybridisation) coordination entities. $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are inner orbital complexes. While $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are outer orbital complex.

Limitations of VBT

Although valence bond theory is advantageous to explain formation, structures and magnetic properties of coordination compounds but it comes with few limitations, listed as follows:

(i) It is based on the number of assumptions.

(ii) It does not distinguish between weak and strong ligands.

(iii) It does not give quantitative interpretations of magnetic data.

(iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.

(v) It fails to explain relative energies of different shapes.

(vi) It does not explain the colour and spectral properties of the 4-coordination compounds.

(vii) It fails to predict the exact tetrahedral and square planar structures of 4-coordinate complexes.

Description of some important metal complexes using VBT

Ion/Complex	Central metal ion	Configuration of metal ion	Hybridisation of metal ion involved	Geometry of the complex	Number of unpaired electrons	Magnetic behaviour
$[Ti(H_2O)_6)]^{3+}$	Ti^{3+}	d^1	d^2sp^3	Octahedral	1	Paramagnetic
$[V(H_2O)_6]^{3+}$	V^{3+}	d^2	d^2sp^3	Octahedral	2	Paramagnetic
$[Cr(H_2O)_6]^{3+}$	Cr^{3+}	d^3	d^2sp^3	Octahedral	3	Paramagnetic
$[Cr(NH_3)_6]^{3+}$	Cr^{3+}	d^3	d^2sp^3	Octahedral	3	Paramagnetic
$[MnF_6]^{3-}$	Mn^{3+}	d^4	sp^3d^2	Octahedral	4	Paramagnetic
$[Mn(CN)_6]^{3-}$	Mn^{3+}	d^4	d^2sp^3	Octahedral	2	Paramagnetic
$[MnCl_4]^{2-}$	Mn^{2+}	d^5	sp^3	Tetrahedral	5	Paramagnetic
$[FeF_6]^{3-}$	Fe^{3+}	d^5	sp^3d^2	Octahedral	5	Paramagnetic
$[Fe(H_2O)_6]^{3+}$	Fe^{3+}	d^5	sp^3d^2	Octahedral	5	Paramagnetic
$[Fe(CN)_6]^{3-}$	Fe^{3+}	d^5	d^2sp^3	Octahedral	1	Paramagnetic
$[Fe(CN)_6]^{4-}$	Fe^{2+}	d^6	d^2sp^3	Octahedral	0	Diamagnetic
$[FeCl_4]^{2-}$	Fe^{2+}	d^6	sp^3	Tetrahedral	4	Paramagnetic
$[Co(NH_3)_6]^{3+}$	Co^{3+}	d^6	d^2sp^3	Octahedral	0	Diamagnetic
$[CoF_6]^{3-}$	Co^{3+}	d^6	sp^3d^2	Octahedral	4	Paramagnetic
$[Ni(CO)_4]$	Ni	$3d^8, 4s^2$	sp^3	Tetrahedral	0	Diamagnetic
$[Ni(CN)_4]^{2+}$	Ni^{2+}	d^8	dsp^2	Square planar	0	Diamagnetic
$[NiCl_4]^{2-}$	Ni^{2+}	d^8	sp^3	Tetrahedral	2	Paramagnetic
$[Ni(H_2O)_6]^{2+}$	Ni^{2+}	d^8	sp^3d^2	Octahedral	2	Paramagnetic
$[CuCl_4]^{2+}$	Cu^{2+}	d^9	sp^3	Tetrahedral	1	Paramagnetic
$[Zn(NH_3)_4]^{2+}$	Zn^{2+}	d^{10}	sp^3	Tetrahedral	0	Diamagnetic
$[Pt(NH_3)Cl_2]$	Pt^{2+}	d^2	dsp^2	Square planar	0	Diamagnetic

CRYSTAL FIELD THEORY (CFT)

This theory was proposed by H. Bethe and van Vleck in 1930. L. Orgel in 1952, gave a much more satisfactory explanation for the bonding and the properties of complexes. The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand.

The main points of this theory are as follows:

(i) The transition metal ion is surrounded by the ligands with lone pairs of electrons and the complex is a combination of central ion surrounded by other ions or molecules or dipoles, e.g. ligands.

(ii) All types of ligands are regarded as point charges in case of anions and as dipoles in case of neutral molecules.

(iii) The interactions between the metal ion and the negative ends of anion (or ion dipoles) is purely electrostatic, i.e. the bond between the metal and ligand is considered to be 100% ionic.

(iv) The ligands surrounding the metal ion produce electrical field and this electrical field influences the energies of the orbitals of central metal ion, particularly *d*-orbitals.

(v) In the case of free metal ion, all five *d*-orbitals have the same energy. Orbitals having the same energies are called degenerate orbitals.

(vi) The five degenerate *d*-orbitals of the metal ion split into different sets of orbital having different energies in the presence of electrical field of ligands. This is called **crystal field splitting.**

(vii) The number of ligands and their arrangement (geometry) around the central metal ion will have different effect on the relative energies of the five *d*-orbitals. In simple words, the crystals field splitting will be different in different structures having different coordination numbers.

(viii) The magnetic properties, spectra and preference for particular geometry can be explained in terms of splitting of *d*-orbitals in different crystal fields.

To understand the crystal field theory, it is essential to understand the disposition of the five *d*-orbitals in space and the geometrical arrangement of the ligands around the central metal ion, i.e. we have to understand the splitting in different crystal fields.

This concept can be illustrated with the complexes having coordination number 6 and 4 (which are very common).

Crystal Field Splitting in Octahedral Coordination Entities

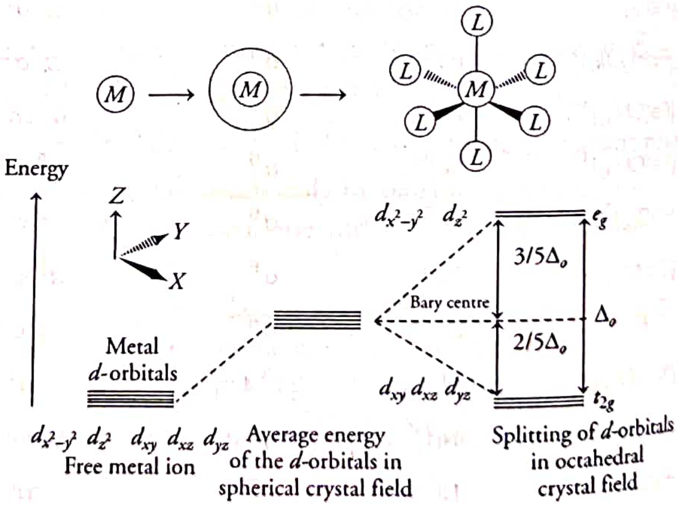
In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal *d*-orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal *d*-orbital is directed towards the ligand than when it is away from the ligand.

Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy and the d_{xy}, d_{zx} and d_{yz} orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field.

Thus, the degeneracy of the *d*-orbitals has been removed due to ligand-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting.

The difference of energy between the two sets of degenerate orbitals as a result of crystal field splitting is known as **Crystal Field Stabilisation Energy** (CFSE), it is denoted by Δ_o (the subscript *o* is for octahedral).

Thus, the energy of the two e_g orbitals will increase by (3/5) Δ_o and that of the three t_{2g} will decrease by $(2/5)\Delta_o$. The splitting of *d*-orbitals in an octahedral crystal field can be seen in following diagram.



d-orbital splitting in an octahedral crystal field

Here, CFSE can be calculated as:

$$CFSE = [-0.4x + 0.6y]\Delta_o$$

where, Δ_o = CFSE in octahedral complex

x = Number of electrons in t_{2g} orbitals

y = Number of unpaired electrons in e_g orbitals

Spectrochemical Series

The crystal field splitting, Δ_o, depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of *d*-orbitals.

So, ligands can be arranged in a series in the order of increasing field strength. This series is known as spectrochemical series.

e.g. $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-}$
$< H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$

It is an experimentally determined series, based on the absorption of light by complexes with different ligands.

The single *d*-electron of metal ion in octahedral coordination entities occupies one of the lower energy t_{2g} orbitals.

In d^2 and d^3 coordination entities, the *d*-electrons occupy the single t_{2g} orbitals in accordance with the Hund's rule.

For d^4 ions, two possible patterns of electron distribution arise:

(i) The fourth electron could either enter the t_{2g} level and pair with an existing electron, or
(ii) It could avoid paying the price of the pairing energy by occupying the e_g level.

These possibilities depend on the relative magnitude of the crystal field splitting, Δ_o and the pairing energy, P (P represents the energy required for electron pairing in a single orbital).

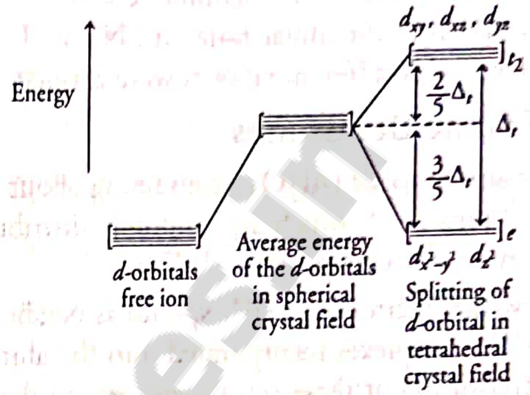
The two options are given below:

(i) If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.
(ii) If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy t_{2g} orbital with configuration $t_{2g}^4 e_g^0$.
Ligands which produce this effect are known as strong field ligands and form low spin complexes.

Calculations show that d^4 to d^7 coordination entities are more stable for strong field as compared to weak field cases.

Crystal Field Splitting in Tetrahedral Coordination Entities

In tetrahedral coordination entity formation, the *d*-orbital splitting is inverted and is smaller as compared to the octahedral field splitting. It can be easily illustrated from the given figure.



d-orbital splitting in a tetrahedral crystal field

Here, CFSE can be calculated as:

$$CFSE = [-0.6x + 0.4y]\Delta_t$$

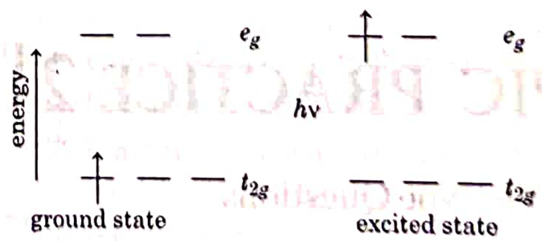
where, Δ_t = CFSE in tetrahedral complex
x = Number of electons in *e*-orbitals.
y = Number of electrons in t_2-orbitals.

For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\Delta_o$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

Colour In Coordination Compounds

When light of certain frequency falls on the complex, it absorbs light from visible range for transition of electron from lower to higher level. Colour of the compound is complementary to the colour of absorbed light. This is known as *d-d* transition.e.g. The complex $[Ti(H_2O)_6]^{3+}$ appears violet in colour due to the transition of electron from t_{2g} level to the e_g level ($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$).

It can be easily understood by following energy diagram



Transition of an electron in $Ti(H_2O)_6]^{3+}$

It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the substance is colourless, e.g. anhydrous $CuSO_4$ is white, while $CuSO_4 \cdot 5H_2O$ is blue.

Effect of Ligand on the Colour of a Complex

Ligand plays an important role in exhibiting the colour to the complex. This can be easily illustrated by considering the example of $[Ni(H_2O)_6]^{2+}$ complex which forms when nickel (II) chloride is dissolved in water. If the didendate ligand, ethane –1, 2– diamine (en) is progressively added in the molar ratio en : Ni, 1 : 1, 2 : 1, 3 : 1; complexes with different colours were formed.

Colour of Some Gemstones

Ruby is aluminium oxide (Al_2O_3) containing about 0.5-1% Cr^{3+} ions (d^3), which are randomly distributed in positions normally occupied by Al^{3+}.

We may view these chromium (III) species as octahedral chromium (III) complexes incorporated into the alumina lattice, *d-d* transitions at these centres give rise to the colour.

In emerald, Cr^{3+} ions occupy octahedral sites in the mineral beryl ($Be_3Al_2Si_6O_{18}$). The absorption bands seen in the ruby shift to longer wavelength, namely yellow-red and blue, causing emerald to transmit light in the green region.

Limitations of CFT

CFT is successful in explaining the colour, magnetic properties, the effects of weak and strong field ligands in coordination compounds. However, it has the following limitations:

(i) As the ligands are point charges, the anionic ligands should exert the greatest splitting effect. Actually, the anionic ligands are found at the low end of the spectrochemical series.

(ii) CFT treats the metal-ligand bond as purely ionic and it does not take into account the covalent character of bonding between the ligand and the central atom.

Note Valence bond theory consider the *M*—*L* bond as covalent while crystal field theory consider the *M*—*L* bond to be ionic.

TOPIC PRACTICE 2

OBJECTIVE Type Questions

1. Which of the following complex ions is diamagnetic in nature?

(a) $[CoF_6]^{3-}$ (b) $[NiCl_4]^{2-}$
(c) $[Ni(CN)_4]^{2-}$ (d) $[CuC_2l]^{2-}$

2. Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour?

(a) $[Ni(NH_3)_6]^{2+}$ (b) $[Zn(NH_3)_6]^{2+}$
(c) $[Cr(NH_3)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$

3. In $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ number of unpaired electrons is, respectively

(a) 4,5 (b) 0,1
(c) 5,4 (d) 1,2

4. The oxidation state of Ni in $[Ni(CO)_4]$ is

(a) 0 (b) 2
(c) 3 (d) 4 **Delhi 2020**

5. Which one of these statements about $[Co(CN)_6]^{3-}$ is true?

(a) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a low-spin configuration
(b) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a low-spin configuration
(c) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a high-spin cofiguration.
(d) $[Co(CN)_6]^{3-}$ has no nupaired electrons and will be in a high-spin configuration.

6. For d^4 ions, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3e_g^1$, when

(a) $\Delta_o > P$ (b) $\Delta_o < P$
(c) $\Delta_o = P$ (d) $\Delta_o \geq P$

7. Atomic number of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex ions are diamagnetic?

I. $[Co(NH_3)_6]^{3+}$ II. $[Mn(CN)_6]^{3-}$
III. $[Fe(CN)_6]^{4-}$ IV. $[Fe(CN)_6]^{3-}$

Choose the correct option.

(a) II and III (b) I and IV
(c) I and III (d) II and IV

8. Structure of $[Ni(CO)_4]$ is

(a) tetrahedral
(b) square planar
(c) octahedral
(d) None of the above

9. The CFSE for octahedral $[CoCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be **NCERT Exemplar**
(a) 18,000 cm^{-1}
(b) 16,000 cm^{-1}
(c) 8,000 cm^{-1}
(d) 20,000 cm^{-1}

10. The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$ **NCERT Exemplar**
(a) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$
(b) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$
(c) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$
(d) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

VERY SHORT ANSWER Type Questions

11. Arrange the following complex ions in the increasing order of crystal field splitting energy (Δ_o), $[CrCl_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$.

12. Why is CO a stronger ligand than Cl^-?

13. Anhydrous $CuSO_4$ is white while hydrated $CuSO_4$ is blue. Why?

SHORT ANSWER Type I Questions

14. (a) Write the IUPAC name and hydridisation of the complex $[Fe(CN)_6]^{3-}$. **Delhi 2020**
(Given : Atomic number of Fe = 26)
(b) What is the difference between an ambidentate ligand and a chelating ligand?

15. Why do compounds having similar geometry have different magnetic moment? **NCERT Exemplar**

16. Magnetic moment of $[MnCl_4]^{2-}$ is 5.92 BM. Give reason.

17. (i) Write the electronic configurat of ion iron of ion in the following complex ion and predict its magnetic behaviour : $[Fe(H_2O)_6]^{2+}$
(ii) Write the IUPAC name of the coordination complex: $[CoCl_2(en)_2]NO_3$ **CBSE SQP 2021**

18. On the basis of crystal field theory, explain why Co(III) forms paramagnetic octahedral complex with weak field ligands whereas it forms diamagnetic octahedral complex with strong field ligands. **NCERT Exemplar**

19. Why are different colours observed in octahedral and tetrahedral complex for the same metal and same ligands? **NCERT Exemplar**

20. What is the relationship between observed colour of the complex and the wavelength of light absorbed by the complex? **NCERT Exemplar**

SHORT ANSWER Type II Questions

21. For the complex $[NiCl_4]^{2-}$, write
(i) the IUPAC name.
(ii) the hybridisation type.
(iii) the shape of the complex.
(Atomic number of Ni = 28) **All India 2013**

22. (i) Predict the geometry of $[NiCN_4]^{2-}$.
(ii) Calculate the spin only magnetic moment of $[Cu(NH_3)_4]^{2+}$ ion. **CBSE SQP 2021**

23. Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex. **NCERT Intext**

24. Answer the following questions.
(i) $[Ni(H_2O)_6]^{2+}(aq)$ is green in colour whereas $[Ni(H_2O)_4(en)]^{2+}(aq)$ is blue in colour, give reason in support of your answer.
(ii) Write the formula and hybridisation of the following compound.
tris-(ethane-1,2-diamine) cobalt(III) sulphate

25. (a) Write the formula of the following coordination compound:
Iron (III) hexacyanoferrate(II)
(b) What type of isomerism is exhibited by the complex $[Co(NH_3)_5Cl]SO_4$?
(c) Write the hybridisation and number of unpaired electrons in the complex $[CoF_6]^{-3}$.
(Atomic number of Co = 27) **CBSE 2018**

26. (i) What type of isomerism is shown by the complex $[Co(NH_3)_5(SCN)]^{2+}$?
(ii) Why $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic?
(Atomic number of Ni = 28)

(iii) Why are low spin tetrahedral complexes rarely observed? **All India 2017**

Or Why are low spin tetrahedral complexes not formed? **Delhi 2017**

27. (i) What type of isomerism is shown by the complex $[Co(en)_3]Cl_3$?

(ii) Write the hybridisation and magnetic character of $[Co(C_2O_4)_3]^{3-}$. (Atomic number of Co = 27)

(iii) Write IUPAC name of the following complex $[Cr(NH_3)_3Cl_3]$.

28. Amongst the following ions which one has the highest magnetic moment value?

(i) $[Cr(H_2O)_6]^{3+}$ (ii) $[Fe(H_2O)_6]^{2+}$

(iii) $[Zn(H_2O)_6]^{2+}$ **NCERT**

29. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why? **NCERT Intext**

30. $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Why? **NCERT**

31. For the complex ion $[CoF_6]^{3-}$, write the hybridisation type, magnetic character and spin nature. [Atomic number : Co = 27] **Delhi 2017**

32. For the complex ion $[Fe(en)_2Cl_2]^+$, write the hybridisation type and magnetic behaviour. Draw one of the geometrical isomer of the complex ion which is optically active.
[Atomic No. : Fe = 26] **All India 2017**

33. In a coordination entity, the electronic configuration of the central metal ion is $t_{2g}^3 e_g^1$.

(i) Is the coordination compound a high spin or low spin complex?

(ii) Draw the crystal field splitting diagram for the above complex.

34. What is the crystal field stabilisation energy? How does the magnitude of Δ_o decide the actual configuration of d-orbital in a coordination entity? **NCERT**

Or What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when **All India 2013**

(i) $\Delta_o > P$ (ii) $\Delta_o < P$

35. The hexaaquamanganese (II) ion contains five unpaired electrons, while the hexacyano ion contains only one paired electron. Explain using crystal field theory. **NCERT Intext**

36. Give the electronic configuration of the following complexes on the basis of crystal field splitting theory. $[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Cu(NH_3)_6]^{2+}$.

37. (i) What type of isomerism is shown by the complex $[Co(NH_3)_6][Cr(CN)_6]$?

(ii) Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless?

(iii) Write the IUPAC name of the following complex : $[Co(NH_3)_5(CO_3)]Cl$ **Delhi 2017**

38. $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why? **NCERT; Foreign 2012**

LONG ANSWER TYPE QUESTIONS

39. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory. **NCERT**

(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$

(iii) $[Co(C_2O_4)_3]^{3-}$ (iv) $[CoF_6]^{3-}$

40. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex.

(i) $K[Cr(H_2O)_2(C_2O_4)_2]\cdot 3H_2O$

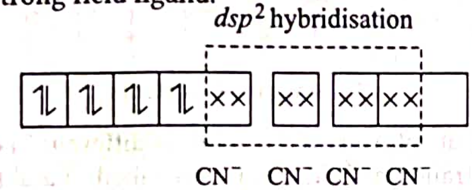
(ii) $[Co(NH_3)_5Cl]Cl_2$ (iii) $[CrCl_3(py)_3]$

(iv) $Cs[FeCl_4]$ (v) $K_4[Mn(CN)_6]$ **NCERT**

41. Write the important postulates and the limitations of valence bond theory.

HINTS AND EXPLANATIONS

1. (c) In $[Ni(CN)_4]^{2-}$, Ni has dsp^2 hybridisation where CN^- is a strong field ligand.

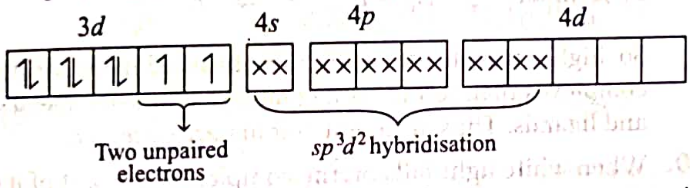


Since, all the electrons are paired, it is diamagnetic.

2. (a) Outer orbital complex utilises d-orbitals for bonding and exhibit paramagnetic behaviour, only if there present unpaired electrons.

In $[Ni(NH_3)_6]^{2+}$, Ni^{2+} = [Ar] $3d^8 4s^0$

$[Ni(NH_3)_6]^{2+}$=



So, this is an outer orbital complex having paramagnetic character.

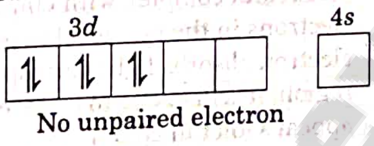
3. (b) Electronic configuration of

Fe_{26} is = [Ar] $3d^6, 4s^2$

Fe^{2+}= [Ar]$3d^6 4s^0$

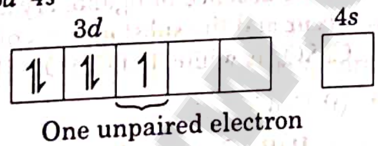
Fe^{3+}= [Ar]$3d^5 4s^0$

$[Fe(CN)_6]^{4-}$ = [Ar]



Fe^{3+} = [Ar] $3d^5 4s^0$

$[Fe(CN)_6]^{3-}$ = [Ar]



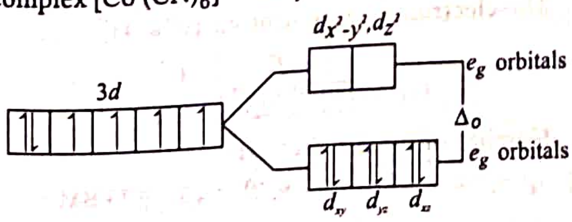
In these complexes, CN^- is a strong field ligand thus electrons get paired.

4. (a) The oxidation state of Ni in $[Ni(CO)_4]$ is 0 as CO is a neutral ligand.

5. (a) $[Co(CN)_6]^{3-}$

Co^{3+}= $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6$

CN^- is a strong field ligand and as it approaches the metal ion, the electron must pair up. The splitting of the d-orbitals into two sets of orbitals in as octahedral complex $[Co(CN)_6]^{3-}$ may be represented as



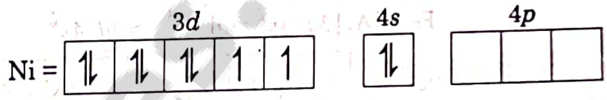
Here, for d^6 ions, three electrons first inter orbitals with parallel spin out the remaining may pair up in t_{2g} orbital giving rise to low spin complex (strong ligand) field.

$\therefore$ $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in low spin configuration.

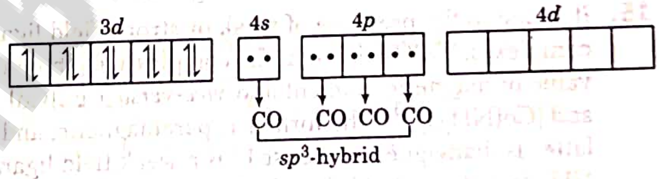
6. (b) The fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$ when $\Delta_o < P$.

7. (c) $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{4-}$, inner orbital complex ions are diamagnetic.

8. (a) In $Ni(CO)_4$ electronic configuration of Ni_{28} = [Ar] $3d^8 4s^2$.



The ligand field of CO influence the arrangement of electrons and shift both 4s electrons into 3d. Now to accomodate electron pairs from 4CO, we have 4s and three 4p-orbital available, this is known as sp^3-hybrid.



9. (c) CFSE for octahedral and tetrahedral complexes are closely related to each other by formula $\Delta_t = \frac{4}{9}\Delta_o$.

where, Δ_o = CFSE for octahedral complex, Δ_t = CFSE for tetrahedral complex

According to question, Δ_o = 18,000 cm^{-1}

$$\therefore \quad \Delta_t = \frac{4}{9}\Delta_o = \frac{4}{9} \times 18{,}000 \text{ cm}^{-1}$$

$$= 4 \times 2{,}000 = 8{,}000 \text{ cm}^{-1}$$

Hence, correct choice is (c).

10. (c) As we know that, strong field ligand split the five degenerate energy levels with more energy separation than weak field ligand, i.e. as strength of ligand increases, crystal field splitting energy increases.

Hence, $$\Delta E = \frac{hc}{\lambda}$$

$$\Rightarrow \quad \Delta E \propto \frac{1}{\lambda}$$

$$\Rightarrow \quad \lambda \propto \frac{1}{\Delta E}$$

As energy separation increases, the wavelength decreases. Thus, the correct order is

$$[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$$

Here, strength of ligand increases, ΔE increases, CFSE increases and λ absored decreases.

Hence, correct choice is (c).

11. CFSE is higher when the complex contains strong field ligand as per spectrochemical series. Thus, crystal field splitting energy increases in the order

$$[CrCl_6]^{3-} < [Cr(NH_3)_6]^{3+} < [Cr(CN)_6]^{3-}$$

Because the order of field strength is $Cl^- < NH_3 < CN^-$

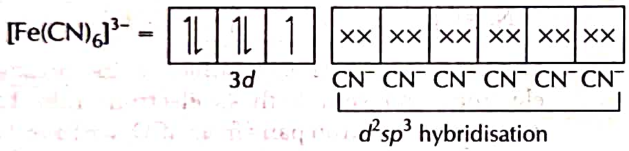
12. It is because CO can form σ (sigma) as well as π-bond therefore, it is stronger ligand than Cl^-.

13. Anhydrous copper sulphate has no ligands while hydrated salt has water as ligand. *d-d* transition is possible in $CuSO_4 \cdot 5H_2O$. So, it is a coloured complex.

14. (*a*) IUPAC name of the complex $[Fe(CN)_6]^{3-}$ is Hexacyanoferrate (III)

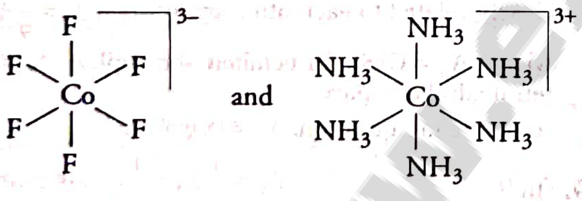
For hybridisation of $[Fe(CN)_6]^{3-}$ In this complex, Fe is present as Fe^{3+}.

$$Fe = [Ar]3d^6 4s^2 \text{ and } Fe^{3+} = 3d^5 4s^0$$



(b) Refer to page 171 and 172. (Ligands)

15. It is due to the presence of weak or strong field ligands in complexes. If CFSE is high, the complex will show low value of magnetic moment and *vice-versa*, e.g. $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$, the former is paramagnetic, and the latter is diamagnetic because F^- is a weak field ligand and NH_3 is a strong field ligand while both have similar geometry.

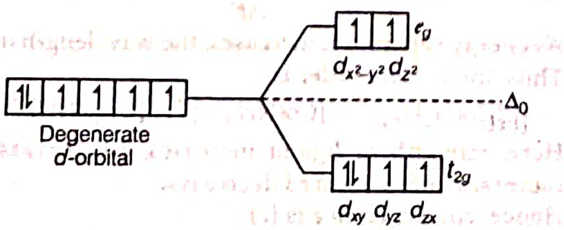


16. The magnetic moment 5.92 BM, shows that there are five unpaired electrons present in the *d*-orbitals of Mn^{2+} ion. As a result, the hybridisation involved is sp^3 rather than dsp^2. Thus, tetrahedral structure of $[MnCl_4]^{2-}$ complex will show 5.92 BM magnetic moment value.

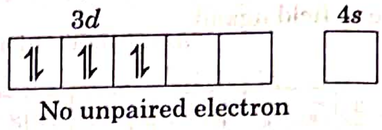
17. (i) Refer to text on page 185.

(ii) The IUPAC name of the coordination complex $[CoCl_2(en)_2]NO_3$ is dichlorido-*bis* (ethane-1, 2-diamine) cobalt (III) nitrate.

18. With weak field ligands, $\Delta_o < P$, (pairing energy) so, the electronic configuration of Co (III) will be $t_{2g}^4 e_g^2$, i.e. it has 4 unpaired electrons and is paramagnetic.



With strong field ligands $\Delta_o > P$ (pairing energy), so pairing occurs thus, the electronic configuration will be $t_{2g}^6 e_g^0$. It has no unpaired electrons and is diamagnetic.



19. Extent of splitting of *d*-orbitals is different in octahedral and tetrahedral field. CFSE in octahedral and tetrahedral are closely related as: $\Delta_t = \left(\frac{4}{9}\right)\Delta_o$

where, Δ_t = crystal field splitting energy in tetrahedral field

Δ_o = crystal field splitting energy in octahedral field

Wavelength of light and CFSE are related to each other by formula $\Delta_o = E = \frac{hc}{\lambda} \Rightarrow E \propto \frac{1}{\lambda}$

So, higher wavelength of light is absorbed in octahedral complexes than tetrahedral complexes for same metal and ligands. Thus, different colours are observed.

20. When white light falls on the complex, some part of it is absorbed. Higher the crystal field splitting energy, lower will be the wavelength absorbed by the complex. The observed colour of complex is the colour generated from the wavelength left over.

e.g. If green light is absorbed, the complex appears red.

In terms of crystal field theory, suppose there is an octahedral complex with empty e_g level and unpaired electrons in the t_{2g} level in ground level. If the unpaired electron absorbs light corresponding to blue-green region, it will excite to e_g level and the complex will appear violet in colour.

In the absence of ligand, crystal field splitting does not occur and the substance is colourless. e.g. Anhydrous $CuSO_4$ is white, but $CuSO_4 \cdot 5H_2O$ is blue in colour.

21. (i) $[NiCl_4]^{2-}$

IUPAC name Tetrachloridonickelate (II) ion

(ii) $Ni^{2+} = 3d^8, 4s^0$

Refer to text on page 184.

(Cl^- being a weak field ligand cannot pair up the unpaired electrons of Ni.)

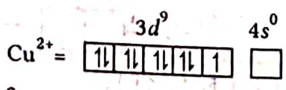
So, it is sp^3 hybridised.

(iii) Because of sp^3 hybridisation, it has tetrahedral geometry.

22. (i) $Ni(CN)_4^{2-}$: Refer to text on page 184.

(ii) In $[Cu(NH_3)_4]^{2+}$ ion, copper is in +2 state.

The electronic configuration is $3d^9 4s^0$.



Number of unpaired electron = 1

$$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$

23. $[Co(NH_3)_6]^{3+}$: Refer to text on page 184.

$[Ni(NH_3)_6]^{2+}$ =

3d: ⇅ ⇅ ⇅ 1 1 | ×× ×× ×× ×× ×× ×× | 4d: □ □ □

$\underbrace{\times\times\ \times\times\ \times\times\ \times\times\ \times\times\ \times\times}_{sp^3d^2 \text{ hybridised}}$

Since, $(n-1)$ d-orbitals are not available. So, the nd-orbitals are used in bond formation, i.e. in hybridisation, the complex is called outer orbital complex.

24. (i) Ligands play an important role in exhibiting the colour to the complex. H_2O is a weak field ligand, which causes small d-d splitting and correspondingly complex give green colour, whereas, ethane-1, 2- diamine (en) is a strong field ligand due to which d-d splitting is increased and correspondingly complex give blue colour.

(ii) **Formula :** $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$

Hybridisation : d^2sp^3

25. (a) Iron (III) hexacyanoferrate (II) has formula—$Fe_4[Fe(CN)_6]_3$

(b) $[Co(NH_3)_5Cl]\,SO_4$ exhibit ionisation isomers. Its ionisation isomer is $[Co(NH_3)_5SO_4]\,Cl$

(c) $[CoF_6]^{3-}$: Oxidation state of cobalt is +3.

Orbitals of Co^{3+} ion: 3d: ⇅ 1 1 1 1 | 4s: □ | 4p: □ □ □ | 4d: □ □ □ □ □

sp^3d^2-hybridised orbitals of Co^{3+}: 3d: ⇅ 1 1 1 1 | 4s: □ | 4p: □ □ □ | 4d: □ □ □ □ □

$[CoF_6]^{3-}$ (outer orbital or high spin complex): 3d: ⇅ 1 1 1 1 | ×× ×× ×× ×× ×× ×× (Six pairs of e^- from 6 F^- ions) | 4d: □ □

Six pairs of electrons one from each F^- ion occupy the six hybrid orbitals. Thus, the complex has octahedral geometry (sp^3d^2).

26. Linkage isomerism arises in a coordination compound containing ambidentate ligand. Hence,

(i) $[Co(NH_3)_5(SCN)]^{2+}$ exhibit linkage isomerism due to presence of SCN which is an ambidentate ligand and can linked with metal either through N or S.

$[Co(NH_3)_5SCN]^{2+}$ and $[Co(NH_3)_5NCS]^{2+}$

(ii) The complex in which one or more unpaired electrons are present is paramagnetic while those which does not contain any unpaired electron is diamagnetic.

Ni atom $(Z=28)$ $3d^84s^2$ = 3d: ⇅ ⇅ ⇅ 1 1 | 4s: ⇅ | 4p: □ □ □

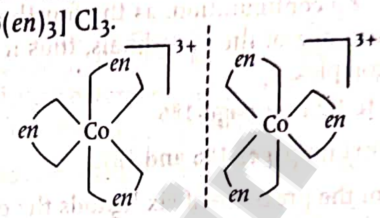
Oxidation state of Ni is + 2 in both the complexes i.e. $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$.

Ni^{2+} = 3d: ⇅ ⇅ ⇅ 1 1 | 4s: □ | 4p: □ □ □

In case of $[NiCl_4]^{2-}$, Cl^- is a weak field ligand so pairing of electrons in 3d-orbital does not occur, hence compound is paramagnetic with two unpaired electrons. In $[Ni(CN)_4]^{2-}$, CN^- is a strong field ligand, hence pairing occurs and $[Ni(CN)_4]^{2-}$ is diamagnetic.

(iii) For tetrahedral complexes, the crystal field stabilisation energy is lower than pairing energy, so they are rarely formed in low spin state.

27. (i) Optical isomerism is shown by the complex $[Co(en)_3]\,Cl_3$.



(ii) In $[Co(C_2O_4)_3]^{3-}$, cobalt is in +3 oxidation state

Co $= [Ar]\,3d^74s^2$

$Co^{3+} = 3d^6\,4s^0$

Co^{3+} = $3d^6$: ⇅ 1 1 1 1 | 4s: □ | 4p: □ □ □

$[Co(C_2O_4)_3]^{3-}$ = $3d^6$: ⇅ ⇅ ⇅ □ □ | 4s: □ | 4p: □ □ □ (d^2sp^3-hybridisation)

Magnetic character = Diamagnetic (all electrons are paired)

(iii) IUPAC name of the complex $[Cr(NH_3)_3Cl_3]$ Triaminetrichloridochromium (III).

28. Electronic configuration of

(i) $Cr^{3+} = 3d^3$, unpaired $e^-(n) = 3$

(ii) $Fe^{2+} = 3d^6$, $n = 4$

(iii) $Zn^{2+} = 3d^{10}$, $n = 0$

From $\mu = \sqrt{n(n+2)}$ BM

Fe^{2+} has the highest magnetic moment value.

29. In $[NiCl_4]^{2-}$, Ni is +2 oxidation state with the configuration in $3d^84s^0$. Cl^- is a weak ligand. It cannot pair up the electrons in 3d orbitals. Hence, it is paramagnetic. In $[Ni(CO)_4]$, Ni is in zero oxidation state with the configuration $3d^8\,4s^2$. In the presence of CO ligand, the 4s electrons shift to 3d to pair up 3d electrons. Thus, there is no unpaired electron present. Hence, it is diamagnetic.

30. Refer to text on page 184 and 185.

31. Refer to text on page 183.

32. In complex $[Fe(en)_2Cl_2]^+$, Fe is in +3 oxidation state

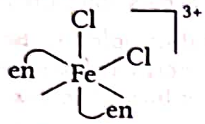
$Fe = 3d^64s^2$ $Fe^{3+} = 3d^5$

= 3d: 1 1 1 1 1 | 4s: □ | 4p: □ □ □

$[Fe(en)_2Cl_2]^+$ = 3d: ⇅ ⇅ 1 | ×× ×× ×× ×× ×× ×× (d^2sp^3 hybridised)

Magnetic character : Paramagnetic

The geometrical isomer of the complex ion which is optically active is



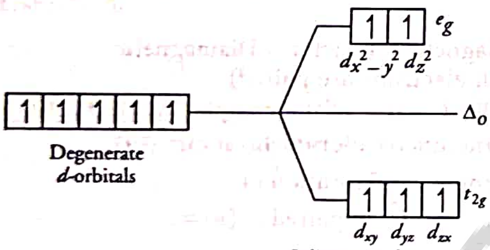
33. (i) In $t_{2g}{}^3\ e_g{}^1$ configuration, as the fourth electron enters in one of the e_g- orbitals, thus it is a high spin complex.

(ii) Refer to text on page 186.

34. Refer to text on pages 186 and 187.

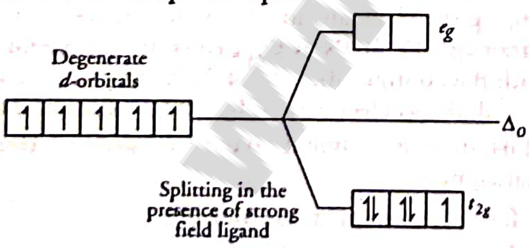
35. Because of the presence of six ligands the complex is octahedral and thus, d-orbital split up into lower energy t_{2g} orbitals and higher energy e_g orbitals.

CN^- is a strong field ligand (thus, causes pairing) and H_2O is a weak field ligand. Mn (II) ion has $3d^5$ configuration. In the presence of H_2O molecules (acting as weak field ligand), the distribution of these five electrons is t_{2g}^3, e_g^2, i.e. all the electrons remain unpaired to form a high spin complex.



Splitting in the presence of octahedral weak field

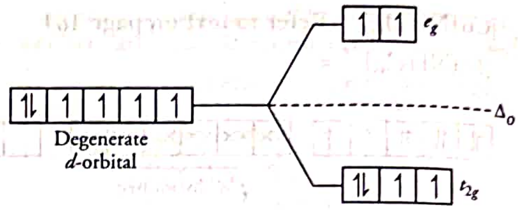
However, in the presence of CN^- (acting as strong field ligands), the distribution of these electrons is t_{2g}^5, e_g^0, i.e. two t_{2g} orbitals contain paired electrons, while the third t_{2g} orbital contains one unpaired electron.The complex formed is a low spin complex.



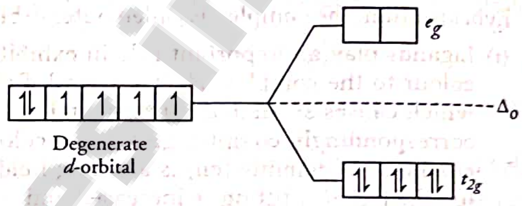
36. According to spectrochemical series, ligands can be arranged in a series in the order of increasing field strength i.e. $F^- < NH_3 < CN^-$.

Hence, CN^- and NH_3 being strong field ligand pair up the t_{2g} electrons before filling e_g set.

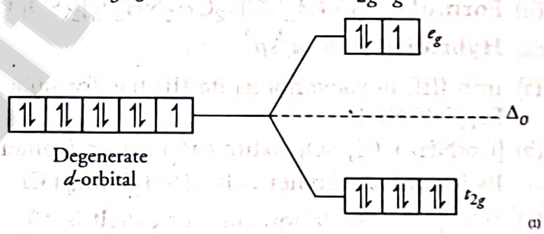
In $[CoF_6]^{3-}$, $Co^{3+} = d^6 \Rightarrow t_{2g}^4, e_g^2$



In $[Fe(CN)_6]^{4-}$, $Fe^{2+} = d^6 \Rightarrow t_{2g}^6 e_g^0$

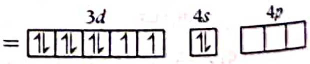


In $[Cu(NH_3)_6]^{2+}$, $Cu^{2+} = d^9 \Rightarrow t_{2g}^6 e_g^3$

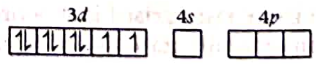


37. (i) The type of isomerism exhibited by the $[Co(NH_3)_6][Cr(CN)_6]$ is coordination isomerism. Here, both the positive and negative ions are complex ions. Isomerism may be caused by the interchange of ligands between the anion and cation. The two isomers are $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6]\ [Co(CN)_6]$

(ii) Electronic configuration of Ni = $[Ar]3d^8 4s^2$ (Z = 28)

Ni atom (Z=28) $3d^8 4s^2$ = 

Oxidation state of Ni is +2 in both $[Ni(H_2O)_6]^{2+}$ and $[Ni(CN)_4]^{2-}$

Ni^{2+} = 

In case of $[Ni(H_2O)_6]^{2+}$, H_2O is a weak field ligand so pairing of electrons in $3d$-orbital does not occur. These unpaired electrons get excited from a lower energy d-orbital to a higher energy d-orbital. Due to d-d transition, $[Ni(H_2O)_6]^{2+}$ possess green colour, whereas CN^- is a strong field ligand so pairing occurs and a solution of $[Ni(CN)_4]^{2-}$ is colourless.

(iii) The IUPAC name of the complex $[Co(NH_3)_5(CO_3)]Cl$ is pentaamminecarbonatocobalt (III) chloride.

38. In both the complex compounds, Fe is in +2 oxidation state with configuration $3d^6$, i.e. it has four unpaired electrons.

In the presence of weak H_2O ligands, the unpaired electrons do not pair up but in the presence of strong ligand CN^-, they get paired up.

Then no unpaired electron is left. Due to this difference in the number of unpaired electrons, both complex ions have different colours.

$[Fe(CN)_6]^{4-}$ = 3d: ⇅ ⇅ ⇅ ⇅ | ×× ×× ×× ×× | 3p: □

CN^- CN^- CN^- CN^-

dsp^2 hybridisation

Square planar structure

39. (i) $[Fe(CN)_6]^{4-}$: In this complex, Fe is present as Fe^{2+}.

$$Fe = [Ar]\,3d^6 4s^2$$

Outer configuration of $Fe^{2+} = 3d^6 4s^0$

$$= \underset{3d^6}{⇅\;1\;1\;1\;1}$$

CN^- being strong field ligand, pair up the unpaired d-electrons. Thus, two $3d$-orbitals are now available for CN^- ions.

$[Fe(CN)_6]^{4-}$ = $3d^6$: ⇅ ⇅ ⇅ | 3d: ×× ×× | 4s: ×× | 4p: ×× ×× ××

No unpaired electron | CN^- CN^- CN^- CN^- CN^- CN^-

d^2sp^3-hybridised

Since, all the electrons are paired, the complex is diamagnetic. Moreover, $(n-1)$ d-orbitals are involved in bonding. So, it is an inner orbital or low spin complex.

(ii) $[FeF_6]^{3-}$ In this complex, the oxidation state of Fe is + 3. $Fe^{3+} = 3d^5 4s^0$

Fe^{3+} = $3d^5$: 1 1 1 1 1 | 4s: □ | 4p: □ □ □ | 4d: □ □ □ □ □

F^- is a weak field ligand, so no pairing occurs. Thus, $3d$-orbitals are not available to take part in bonding.

$[FeF_6]^{3-}$ =

3d: 1 1 1 1 1 | ×× ×× ×× ×× ×× ×× | 4d: □ □ □

sp^3d^2-hybridised

Because of the presence of five unpaired electrons, the complex is paramagnetic. Moreover, nd-orbitals are involved in bonding, so it is an outer orbital or high spin complex.

(iii) $[Co(C_2O_4)_3]^{3-}$ In this complex, the oxidation state of Co is +3.

Outer configuration of $Co = 3d^7 4s^2$

$$Co^{3+} = 3d^6\,4s^0$$

Co^{3+} = $3d^6$: ⇅ 1 1 1 1 | $4s^0$: □

Oxalate ion being a strong field ligand pair up the $3d$-electrons, thus two out of the five $3d$-orbitals are available for oxalate ions.

$[Co(C_2O_4)_3]^{3-}$ = 3d: ⇅ ⇅ ⇅ | ×× ×× ×× ×× ×× ××

d^2sp^3 hybridised

Since, all the electrons are paired, hence this complex is diamagnetic. It is an inner orbital complex because of the involvement of $(n-1)$ d-orbital for bonding.

(iv) Refer to text on page 183.

40. (i) Potassium diaquadioxalatochromate(III) hydrate

CN = 6

Shape = octahedral

Oxidation state of

$$Cr = x + 0 + 2 \times (-2) = -1$$
$$x = 3$$

E.C of $Cr^{3+} = 3d^3$ or $t_{2g}^3 e_g^0$

Unpaired electrons $(n) = 3$

Magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM

$$= \sqrt{3 \times 5} = 3.87 \text{ BM}$$

(ii) Pentaamminechloridocobalt (III) chloride

CN of Co = 6

Shape = octahedral

OS of Co = +3

$$Co^{3+} = 3d^6 \text{ or } t_{2g}^6\, e_g^0$$

Number of unpaired electrons $(n) = 0$

$$\mu = 0$$

(iii) Trichloridotripyridinechromium (III)

Coordination no. of Cr = 6.

Shape = Octahedral

Oxidation state Cr : $x - 3 + 0 = 0$, $x = +3$

E.C. of $Cr^{3+} = 3d^3 = t_{2g}^3 e_g^0$, $n = 3$, $\mu = 3.87$ BM.

(iv) Caesium tetrachloridoferrate (III)

CN of Fe = 4,

Shape = tetrahedral

OS of Fe = + 3

$$Fe^{3+} = 3d^5 \text{ or } t_{2g}^3 e_g^2$$

Number of unpaired electons $(n) = 5$,

$$\mu = \sqrt{5(5+2)} \text{ BM}$$
$$\mu = 5.92 \text{ BM}$$

(v) Potassium hexacyanomanganate (II)

CN of Mn = 6,

Shape = octahedral

OS of Mn = + 2

$$Mn^{2+} = 3d^5 \text{ or } t_{2g}^5\, e_g^0,$$

Number of unpaired electons $(n) = 1$,

$$\mu = 1.73 \text{ BM}$$

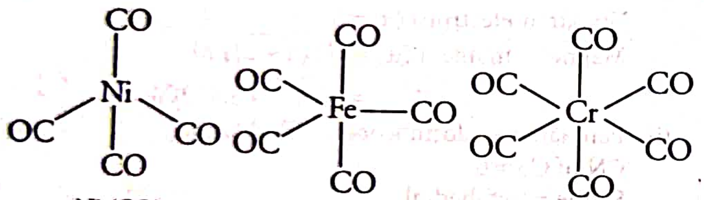
41. Refer to text on pages 183 and 185.

|TOPIC 3|

Metal Carbonyls, Stability and Significance of Coordination Compounds

METAL CARBONYLS

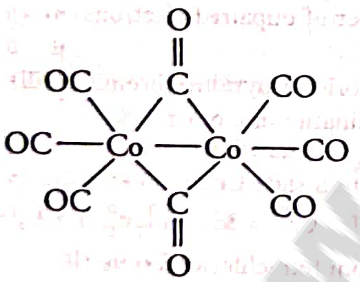
Compounds of transition metal with carbonyls (carbon monoxide), are known as metal carbonyls. These carbonyls have simple well defined structure. Tetracarbonylnickel (0) is tetrahedral, pentacarbonyliron (0) is trigonal bipyramidal while hexacarbonyl chromium (0) is octahedral. Decacarbonyldimanganese (0) is made up of two square pyramidal, $Mn(CO)_5$ units joined by Mn—Mn bond. Octacarbonyldicobalt(0) has a Co—Co bond bridged by two CO groups. It is of two types, i.e. mononuclear and polynuclear. The structures of some metal carbonyls are given below :



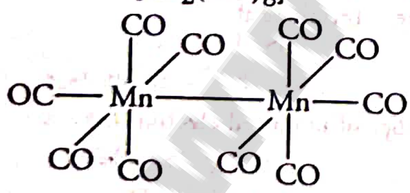
$Ni(CO)_4$ Tetrahedral

$Fe(CO)_5$ Trigonal bipyramidal

$Cr(CO)_6$ Octahedral



$[Co_2(CO)_8]$

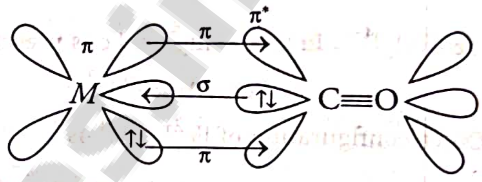


$[Mn_2(CO)_{10}]$

Structures of some representative homoleptic metal carbonyls

Bonding in Metal Carbonyls

The metal-carbon bond in metal carbonyls possess both σ and π-character. The M—C σ-bond is formed by the donation of lone pair of electrons of the carbonyl carbon into a vacant orbital of the metal. The M—C π-bond is formed by the donation of a pair of electrons from a filled d-orbital of metal into vacant antibonding π^* orbital of carbon monoxide. The M—L bonding creates a synergic effect which strengthens the bond between CO and the metal.



Synergic bonding

STABILITY OF COORDINATION COMPOUNDS

The stability of a complex or coordination compound refers to the extent upto which it exists in a solution as coordination sphere. Factors affecting the stability of complex are :

(i) **Charge on the central metal ion** Greater the charge on the central metal ion, greater the stability of complex.

(ii) **Nature of the metal ion** Groups 3 and 6 and inner transition elements form stable complexes when donor atoms of the ligands are N, O and F. The elements after group 6 of the transition metals form stable complexes when the donor atoms of the ligands are the heavier members of N, O and F family.

(iii) **Basic nature of the ligands** Greater the basic strength, greater is the stability of the complex.

(iv) **Presence of chelate rings** Its presence increases the stability of the complex. It is called chelate effect. It is maximum for the 5 and 6 membered rings.

(v) **Effect of multidentate cyclic ligands** If the ligands are π multidentate and cyclic without any steric effect, the stability of the complex get increased.

Stability Constant

Stability of a complex is measured in terms of stability constant. It is actually the magnitude of equilibrium constant of the complex formation reaction.
It is of two types :

(a) Stepwise Stability Constant

A complex is formed in a stepwise additive attachment of ligand to the metal. Equilibrium constant for every step is known as stepwise stability constant of a complex and is denoted by K_n (where, n can take any integer value from 1 to infinity).

(b) Overall Stability Constant

The equilibrium constant of overall formation of complex in a reaction is called overall stability constant denoted by β.

It is given as:

$$[M(H_2O)_n] + nL \longrightarrow ML_n + nH_2O$$

$$\beta_n = \frac{[ML_n]}{[M(H_2O)_n][L]^n}$$

Consider the following chemical reaction

$$M + 4L \rightleftharpoons ML_4; \beta_4 = [ML_4]/[M][L]^4$$

where, β_4 is the overall stability constant.

Overall stability constant is the equilibrium constant for net reaction. The stepwise stability constant can be given as:

$$M + L \rightleftharpoons ML, k_1 = [ML]/[M][L]$$
$$ML + L \rightleftharpoons ML_2, k_2 = [ML_2]/[ML][L]$$
$$ML_2 + L \rightleftharpoons ML_3, k_3 = [ML_3]/[ML_2][L]$$
$$ML_3 + L \rightleftharpoons ML_4, k_4 = [ML_4]/[ML_3][L]$$

where, k_1, k_2 etc., are referred to as stepwise stability constants.

The stepwise stability constants and overall constants are related as:

$$\beta_4 = k_1 \times k_2 \times k_3 \times k_4 \text{ or more generally}$$

and $\beta_n = k_1 \times k_2 \times k_3 \times k_4 \cdots k_n$

e.g. $Cu^{2+} + NH_3 \rightleftharpoons Cu(NH_3)^{2+}$,

$$k_1 = [Cu(NH_3)^{2+}]/[Cu^{2+}][NH_3]$$

$$Cu(NH_3)^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_2^{2+},$$

$$k_2 = [Cu(NH_3)_2^{2+}]/[Cu(NH_3)]^{2+}[NH_3], \text{ etc.}$$

Also, $\beta_4 = [Cu(NH_3)_4^{2+}]/[Cu^{2+}][NH_3]^4$

SIGNIFICANCE OF COORDINATION COMPOUNDS

Due to their complex structures, coordination compounds hold very important significance in the natural as well as man-made realms. Important applications of these compounds are discussed below :

1. In Biological Systems

(i) Haemoglobin, the oxygen carrier in blood, is a coordination compound of Fe^{2+} with porphyrin ring.

(ii) The pigment chlorophyll in plants, responsible for photosynthesis, is a coordination compound of Mg^{2+} with porphyrin.

(iii) Vitamin B_{12} also called cobalamin, is a coordination compound of cobalt.

2. In Medicinal Chemistry

(i) The platinum complex *cis*-$[Pt(NH_3)_2Cl_2]$, commonly known as *cis*-platin, is used in the treatment of cancer.

(ii) EDTA complex of calcium is used in the treatment of lead poisoning.

(iii) The excess of copper and iron present in animal system are removed by the chelating ligands D-penicillamine and desferrioxime B *via* the formation of complexes.

3. In Analytical Chemistry

(i) Detection of Cu^{2+}.

(ii) Estimation of hardness of water.

(iii) Ni^{2+} is detected by the formation of a red complex with dimethyl glyoxime (DMG).

(iv) The separation of Ag^+ and Hg^{2+} in group I is based on the fact that AgCl dissolves in NH_3, while Hg_2Cl_2 makes an insoluble black substance with it.

4. In the Extraction/Metallurgy of Metals

(i) Extraction of various metals from their ore involves complex formation, e.g. silver and gold are extracted from their ore by dissolving it in NaCN.

(ii) Also used for the purification of metals, e.g. Mond's process for the purification of nickel, in which impure Ni is converted to $[Ni(CO)_4]$ which is decomposed to yield pure nickel.

5. In other Areas

(i) Electroplating of metals involves the complex salts as electrolyte.

(ii) It is used in homogeneous and heterogeneous catalysis, e.g. Wilkinson catalyst $[(Ph_3P)_3RhCl]$ is used for the hydrogenation of alkenes.

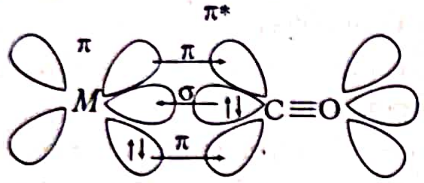
(iii) It is used as an antiknock, e.g. $[(C_2H_5)_4Pb]$.

(iv) In photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.

TOPIC PRACTICE 3

OBJECTIVE Type Questions

1. Consider the following figure.



Which type of bond formed between metal and ligand?

(a) synergic bond (b) σ-bond
(c) π-bond (d) None of these

2. The $M - C\pi$-bond is formed by the
   (a) donation of a pair of electrons
   (b) sharing of a pair of electrons
   (c) receiving a pair of electrons
   (d) None of the above

3. The total number of metal-metal bond present in $[Co_2(CO)_8]$ is
   (a) 0 (b) 3 (c) 2 (d) 1

4. For the reaction of the type $M + 4L \rightleftharpoons ML_4$
   (a) larger the stability constant, lower the proportion of ML_4 that exists in solution
   (b) larger the stability constant, higher the proportion of ML_4 that exists in solution
   (c) smaller the stability constant, higher the proportion of ML_4 that exists in solution
   (d) None of the above

5. The reciprocal of the formation constant is called
   (a) instability constant (b) dissociation constant
   (c) stability constant (d) Both (a) and (b)

6. Which of the following complexes formed by Cu^{2+} ions is most stable? **NCERT Exemplar**
   (a) $Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}, \log K = 11.6$
   (b) $Cu^{2+} + 4CN^- \longrightarrow [Cu(CN)_4]^{2-}, \log K = 27.3$
   (c) $Cu^{2+} + 2en^- \longrightarrow [Cu(en)_2]^{2+}, \log K = 15.4$
   (d) $Cu^{2+} + 4H_2O \longrightarrow [Cu(H_2O)_4]^{2+}, \log K = 8.9$

7. Hardness of water is estimated by simple titration with Na_2 - EDTA because
   (a) Ca^{2+} ions form stable complexes with EDTA
   (b) Mg^{2+} ions form stable complexes with EDTA
   (c) Ca^{2+} ions form unstable complexes with EDTA
   (d) Both (a) and (b)

8. For lead-poisoning, the antidote used is
   (a) white of an egg
   (b) *cis*-platin
   (c) nickel
   (d) EDTA

9. In photography, the use of $Na_2S_2O_3 \cdot 5H_2O$ is
   (a) for converting AgBr into Ag_2SO_4
   (b) for converting AgBr into soluble thiosulphate complex
   (c) for converting AgBr into silver thiosulphate
   (d) in reduction of Ag metal from AgBr

VERY SHORT ANSWER Type Questions

10. Give an example of a metal carbonyl having metal-metal bond.

11. A coordination compound (X) is used in the treatment of cancer. What is 'X' here?

12. Name the complex used as oxygen carrier in the blood.

SHORT ANSWER Type I Questions

13. Discuss the nature of bonding in metal carbonyls. **NCERT**

14. Calculate the overall complex dissociation equilibrium constant for the $[Cu(NH_3)_4]^{2+}$ ions, given that β_4 for this complex is 2.1×10^{13}. **NCERT Intext**

15. Discuss briefly giving an example in each case, the role of coordination compounds in
    (i) biological systems
    (ii) medicinal chemistry
    (iii) analytical chemistry
    (iv) extraction/metallurgy of metals **NCERT**

SHORT ANSWER Type II Questions

16. What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes. **NCERT**

17. Calculate the
    (i) ratio of $[Ag(NH_3)_2]^+$ and $[Ag^+]$ in 0.1 M NH_3 solution.
    (ii) ratio of $[Ag(S_2O_3)_2]^{3-}$ and $[Ag^+]$ in 0.1 M $S_2O_3^{2-}$ solution. Given that the stability/formation constants (K_f) for $[Ag(NH_3)_2]^{2+}$ and $[Ag(S_2O_3)_2]^{3-}$ are 1.7×10^7 and 1.0×10^{13} respectively.

18. Draw the structure of following homoleptic metal carbonyl.
    (i) $[Ni(CO)_4]$ (ii) $[Fe(CO)_5]$ (iii) $Cr(CO)_6$

19. What do you understand by stepwise stability constant and overall stability constant of a coordination compound? How are these two constants related?

20. Give an example for each when coordination compounds play an important role in
 (i) photosynthesis by plant.
 (ii) removal of excess of iron present in our body.
 (iii) development of photographic film.

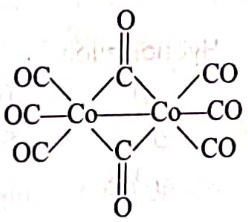
21. Name the following:
 (i) Ring that is attached to Fe^{2+} in haemoglobin.
 (ii) Vitamin B_{12} is a coordination compound of this element.
 (iii) Complex that is used in homogeneous and heterogeneous catalysis.

HINTS AND EXPLANATIONS

1. *(a)* The metal-carbon bond in metal carbonyls possess both σ and π-character. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.

2. *(a)* The M–C π-bond is formed by the donation of a pair of electrons.

3. *(d)*



Total number of metal -metal bond = 1

4. *(b)* For the reaction of the type
$$M + 4L \rightleftharpoons ML_4,$$
larger the stability constant, the higher the proportion of ML_4 that exists in solution.

5. *(d)* The reciprocal of the formation constant is called instability constant or dissociation constant.

6. *(b)* Greater the value of log K, greater will be stability of complex compound formed.
For reaction,
$$Cu^{2+} + 4CN^- \longrightarrow [Cu(CN)_4]^{2-}$$
$$K = \frac{[(Cu(CN)_4)^{2-}]}{[Cu^{2+}][CN^-]^4} \text{ and } \log K = 27.3$$
For this reaction, log K has highest value among the given four reactions. Hence, K will also be higher among these four. i.e. stability of the complexes will be highest among these four complexes.

7. *(d)* Hardness of water is estimated by simple titration with Na_2 EDTA because Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA.

8. *(d)* For lead poisoning, the antidote used is EDTA.

9. *(b)* $AgBr + 2Na_2S_2O_3 \longrightarrow \underset{\text{Soluble complex}}{Na_3[Ag(S_2O_3)_2]} + NaBr$

10. $Mn_2(CO)_{10}$

11. *cis*-platin, $[Pt(NH_3)_2Cl_2]$

12. Haemoglobin.

13. Refer to text on page 196.

14. Dissociation constant is the reciprocal of the stability constant, β_4. Overall complex dissociation equilibrium
$$\text{constant} = \frac{1}{\beta_4}$$
$$= \frac{1}{2.1\times 10^{13}} = 4.7\times 10^{-14}$$

15. Refer to text on page 197.

16. Refer to text on pages 196.

17. (i) The equilibrium set up is
$$Ag^+ + 2NH_3 \xrightleftharpoons{K_f} [Ag(NH_3)_2]^+$$
$$\therefore \text{ Stability constant, } K_f = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2}$$
$$= 1.7\times 10^7 \text{ (given)}$$
$$\text{or } \frac{[Ag(NH_3)_2]^+}{[Ag^+]} = 1.7\times 10^7 \times [NH_3]^2$$
$$= 1.7\times 10^7 \times (0.1)^2 = 1.7\times 10^5$$
(ii) The equilibrium set up is
$$Ag^+ + 2S_2O_3^{2-} \xrightleftharpoons{K_f} [Ag(S_2O_3)_2]^{3-}$$
∴ Stability constant,
$$K_f = \frac{[Ag(S_2O_3)_2]^{3-}}{[Ag^+][S_2O_3^{2-}]^2} = 1.0\times 10^{13} \text{(given)}$$
$$\therefore \frac{[Ag(S_2O_3)_2]^{3-}}{[Ag^+]} = 1.0\times 10^{13}\times[S_2O_3^{2-}]^2$$
$$= 1.0\times 10^{13}\times(0.1)^2 = 1\times 10^{11}$$

18. Refer to text on page 196.

19. Refer to text on page 196.

20. (i) Porphyrin (ii) Cobalt
 (iii) Refer to text on page 197.

21. Refer to text on pages 197.

SUMMARY

- Addition compounds are formed when two or more stable compounds combine together in stoichiometric ratio.
- Coordination compounds do not dissociate and retain their identity in solution, e.g. $K_4[Fe(CN)_6]$
- **Double salts** dissociate and lose their identity in solution, e.g. Mohr's salt.
- according to **Werner's theory** primary valency is ionisable but secondary valency is not.
- **Coordination entity** contains central metal atom/ion surrounded by fixed number of ions or molecules.
- Ions/molecules which donate their lone pair of electrons to central metal ion are called **ligands.** They may be positive, negative or neutral.
- On the basis of number of donor atoms present, ligands are classified as monodentate, bidentate or polydentate.
- The number of ligands bonded to the metal is called **coordination number.**

  CN = number of ligands × denticity
- **Oxidation number** is the charge carried by central metal atom/ion if all the ligands are removed.
- **IUPAC Nomenclature**
  - **For Cationic Complexes** : Counter ion name + ligand name with quantity in alphabetical order + metal name + ate + (OS of metal)
  - **For Anionic/Neutral Complexes** : Ligand no. + ligand name (alphabetically) + metal name + (OS of metal) + counter ion name (if present)

    H_2O-aqua, NO-nitrosyl, Cl^- - chlorido, CN^- - cyano, etc
- **Structural isomerism** is due to difference in structural arrangement.
- **Ionisation isomerism** This is shown by isomers which give different ions in solution or in molten state, e.g.

  $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.
- **Linkage isomerism** is due to presence of ambident ligands like NO_2, SCN etc.
- **Coordination isomerism** arises when both the ions are complexes, e.g. $[Co(NH_3)_6][Co(CN)_6]$.
- **Hydrate isomerism** is due to difference in H_2O molecules inside the sphere.
- **Stereoisomers** have same molecular formula but different spatial arrangements.
- **Geometrical isomerism** is shown by complexes of the type MA_2B_2, $MABCD$, MA_2B_4 etc. but not by tetrahedral complexes.
- **Optical isomerism** is shown by complexes having atleast one bidentate ligand.
- **Valence bond theory** (VBT) explains the formation, magnetic behaviour and geometrical shapes of coordination compounds. It fails to provide quantitative interpretation of magnetic properties.

  By this property of a complex can be calculated as:
  - Predict the OS of central metal atom/ion.
  - Write EC of central metal atom/ion.
  - Pair up the d-electron, if ligand is strong like CN^-, CO, NH_3 etc.
  - Fill ligands in empty d-orbitals and predict hybridisations and structure as.

Orbital Used	Hybridisation	Structure
$1s + 3p$	sp^3	Tetrahedral
$1d + 1s + 2p$	dsp^3	Square planar
$2d + 1s + 3p$	sp^3d^2	Octahedral

  - If unpaired electron (s) are present, then paramagnetic otherwise diamagnetic
  - $(n-1)d$ – orbital used by ligand = inner orbital while and d-orbital used by ligand = outer orbital complx.
- **Crystal field theory** (CFT) is based on the effect of different crystal on degeneracy of d-orbital energies of central metal ion.
- Here, d-orbital of metal splits into $d_{x^2-y^2}$, and d_{z^2} (i.e. e_g set) and d_{xy}, d_{yz}, d_{zx} (i.e. t_{2g} set).

  For tetrahedral, $e_g < t_{2g}$; For Octahedral, $e_g > t_{2g}$
  - If $\Delta_0 < P$, then complex is high spin or weak field.
  - If $\Delta_0 < P$, then complex is low spin or strong field.
- CFT provides quantitative estimation of orbital separation energies, magnetic moments and stability parameters.
- **Stability** is measured in terms of stepwise stability constant. A complex is more stable if a metal has more charge.
- **Metal-carbonyl compounds** possess both σ and π-character. The ligand to metal is σ-bond and metal to ligand is π-bond. This synergic bonding provides stability to metal carbonyls.

CHAPTER PRACTICE

OBJECTIVE Type Questions

1 Square planar structure is

(a) $[Ni(CO)_4]$ (b) $[NiCl_4]^{2-}$

(c) $[Ni(CN)_4]^{2-}$ (d) None of these

2 Heterolyptic complex is

(a) $[Fe(CN)_6]^{4-}$ (b) $[Co(NH_3)_5SO_4]^+$

(c) $[HgI_4]^{2-}$ (d) $[Co(NH_3)_6]^{3+}$

3 A magnetic moment of 1.73 BM will be shown by one among the following.

(a) $[Cu(NH_3)_4]^{2+}$ (b) $[Ni(CN)_4]^{2-}$

(c) $TiCl_4$ (d) $[CoCl_6]^{4-}$

4 Among the ligands NH_3, en, CN^- and CO, the correct order of their increasing field strength, is

(a) $CO < NH_3 < en < CN^-$ (b) $NH_3 < en < CN^- < CO$

(c) $CN^- < NH_3 < CO < en$ (d) $en < CN^- < NH_3 < CO$

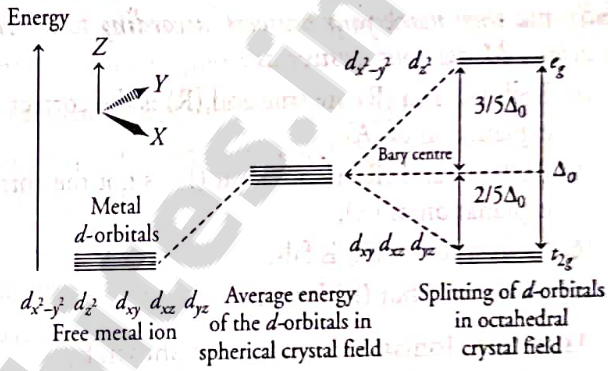
CASE BASED Questions

Case I

Crystal field theory was proposed by H. Bethe and van Vleck in 1930. L. Orgel in 1952, gave a much more satisfactory explanation for the bonding and the properties of complexes. The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d-orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal d-orbital is directed towards the ligand than when it is away from the ligand.

The degeneracy of the d-orbitals has been removed due to ligand-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set.

The splitting of d-orbitals in an octahedral crystal field can be seen in following diagram.



The following questions are multiple choice questions. Choose the most appropriate answer :

5 What is full form of CFSE?

(a) Crystal field stabilisation energy

(b) Crystal field shield energy

(c) Crystal field shield electronegativity

(d) None of the above

6 Which of the following ligand is stronger than Cl^-?

(a) SCN^- (b) CO

(c) Br^- (d) I^-

Or Arrange the following complex ions in the increasing order of crystal field splitting energy.

$\underset{\text{I}}{[CrCl_6]^{3-}}$, $\underset{\text{II}}{[Cr(CN)_6]^{3-}}$, $\underset{\text{III}}{[Cr(NH_3)_6]^{3+}}$.

(a) III < II < I (b) I < III < II

(c) II < I < III (d) I < II < III

7 What is spectrochemical series?

(a) Arrangement of ligand

(b) Order of field strength of ligand

(c) CFSE values order of ligand

(d) All of the above

8 On the basis of CFT, write the electronic configuration of d^4 in an octahedral field when $\Delta_O < P$.

(a) $t_{2g}^2\, e_g^2$ (b) $t_{2g}^1\, e_g^3$

(c) $t_{2g}^3\, e_g^1$ (d) $t_{2g}^4\, e_g^0$

Case II

Isomerism is a phenomenon in which compounds have the same molecular formula but different physical and chemical properties on account of different structures. The two major types of isomerism are structural and stereoisomerism. The structural isomerism is further divided into four types: Linkage, coordination, ionisation and solvate isomerism. While, the stereoisomerism is divided into two types : geometrical and optical isomerism.

In the question that follow Assertion and Reason are given. Reason is purported to the explaination for Assertion. Study carefully and then mark your answers, according to the codes given below. Marks your answer as :

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

9 **Assertion** Ionisation isomerism shown by compounds having same composition.
Reason Compounds having same ions in the solutions.

10 **Assertion** Coordination compounds show linkage isomerism.
Reason They have ambidentate ligands.

Or **Assertion** $[Pt(NH_3)_4][PtCl_4]$ shows coordination isomerism.
Reason It also shows ionisation isomerism.

11 **Assertion** $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$ show ionisation isomerism.
Reason Because they have Co metal.

12 **Assertion** Heteroleptic complexes show geometrical isomerism.
Reason Complexes with coordination number 6 and 8 are heteroleptic.

ASSERTION and REASON

■ **Directions** (Q. Nos. 13-20) *In the following questions, an Assertion (A) is followed by a corresponding Reason (R) Use the following keys to choose the appropriate answer.*

(a) Both (A) and (R) are correct, (R) is the correct explanation of (A).

(b) Both (A) and (R) are correct, (R) is not the correct explanation of (A).

(c) (A) is correct; (R) is incorrect.

(d) (A) is incorrect; (R) is correct.

13 **Assertion** (A) In the coordination compound $[Co(H_2NCH_2CH_2NH_2)_3]_2$, ethane-1,2-diamine is a neutral ligand.
Reason (R) Oxidation number of Co in the complex ion is +3.

14 **Assertion** (A) Isomers differ in one or more physical or chemical properties.
Reason (R) These have different arrangement of atoms.

15 **Assertion** (A) Tetrahedral complexes do not show geometrical isomerism.
Reason (R) The relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other.

16 **Assertion** (A) Oxidation number of Cr in $[Cr(NH_3)_3(H_2O)_3]Cl_3$ is same as the charge of the complex ion, +3.
Reason (R) All the ligands are neutral molecules in this compound.

17 **Assertion** (A) The stability of $[Ni(en)_3]Cl_2$ is lower than that of $[Ni(NH_3)_6]Cl_2$.
Reason (R) The geometry of Ni is trigonal bipyramidal in $[Ni(en)_3]Cl_2$.

18 **Assertion** (A) The ligands of nitro and nitrito are called ambidentate ligands.
Reason (R) These ligands give linkage isomers.

19 **Assertion** (A) $[Ni(CN)_4]^{2-}$ is square planar and dimagnetic.
Reason (R) It has no unpaired electrons due to presence of strong field ligand.

20 **Assertion** (A) The total number of isomers shown by $[Co(en)_2Cl_2]^+$ complex ion is three.
Reason (R) $[Co(en)_2Cl_2]^+$ complex ion has an octahedral geometry.

VERY SHORT ANSWER Type Questions

21 What is the coordination number of Fe in $[Fe(CN)_6]^{4-}$?

22 Write the IUPAC name of $[Co(NH_3)_5ONO]^{2+}$.

23 Write the oxidation number of Pt in
$[PtCl_2(NH_3)_2]$

24 Write the IUPAC name of $[PtCl_6]^{2-}$.

25 How many ions are produced from the complex $[Cr(H_2O)_6]Cl_3$ in solution?

26 Give the examples of two coordination complexes where central metal atom has coordination number
(i) 4 (ii) 6

27 Which type of isomerism is exhibited by $[Co(NH_3)_3(NO_2)_3]$?

28 Give one example for each.
(i) Neutral ligand of carbon
(ii) Positive ligand of nitrogen

29 An element 'X' has one unpaired electron. Calculate its magnetic moment.

30 Write an important factor on which the crystal field splitting depends.

31 Arrange the following complex ions in the increasing order of crystal field splitting energy (Δ_o), $[Fe(CN)_6]^{4-}$, $[Fe(CO)_5]$, $[Fe(en)_3]^{3+}$

32 If an element have high positive charge then what will be its affect on the stability of complex?

SHORT ANSWER Type I Questions

33 Draw all the possible geometrical and optical isomerism of $[Co(NH_3)_2Cl_2(en)]^+$.

34 What is crystal field splitting among octahedral and tetrahedral crystal fields? In which case, the magnitude of crystal field splitting is larger?

35 A complex of the type $[M(AA)_2X_2]^{n+}$ is known to be optically active. What does this indicate about the structure of complex? Give one example of such complex.

36 Write the structures and names of all stereoisomers of the following compounds:
(i) $[Co(en)_3]Cl_3$ (ii) $[Pt(NH_3)_2Cl_2]$

37 The complexes $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $[Cr(NH_3)_6]$ $[Co(CN)_6]$ are the examples of which type of isomerism? State its definition.

38 How many isomers can be formed for the complex $[Co(C_2O_4)_2(NH_3)_2]$?

39 Give the name, the stereochemistry and the magnetic behaviour of the following complexes.
(i) $[Co(NH_3)_5Cl]Cl_2$
(ii) $K_2[Ni(CN)_4]$

40 Give the formula of each of the following coordination compound entities.
(i) Co^{3+} ion is bound to one Cl^-, one NH_3 molecule and two bidentate ethylenediamine (en) molecules.
(ii) Ni^{2+} ion is bound to two water molecules and two oxalate ions.

41 Write the structure of $[Co_2(CO)_8]$ and $[Mn_2(CO)_{10}]$.

42 List down the major factors which affect the stability of coordination complexes.

43 Explain the following.
(i) Complex that is used as an anti-knock.
(ii) Complex of calcium used in the treatment of lead poisoning.

SHORT ANSWER Type II Questions

44 Explain the shape and magnetic behaviour of $[Ni(H_2O)_6]^{2+}$.

45 Draw the diagram showing splitting of d-orbital in tetrahedral complex.

46 Name the compound $[Fe(H_2O)_5NO]^{2+}$ and explain the magnetic properties of $[Fe(H_2O)_5NO]^{2+}$ and oxidation state of iron in this complex.

47 Using valence bond theory, explain the following in relation to the complexes, given below : $[Mn(CN)_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$.
(i) Type of hybridisation
(ii) Magnetic behaviour
(iii) Inner or outer orbital complex

48 Compare the following complexes with respect to structural shapes of units, magnetic behaviour and hybrid orbitals involved in units.
(i) $[Ni(CN)_4]^{2-}$ (ii) $[NiCl_4]^{2-}$ (iii) $[CoF_6]^{3-}$
(Atomic number of Ni = 28, Co = 27)

49 Giving a suitable example for each, explain the following.
(i) Linkage isomerism (ii) Chelating ligand

50 $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$, both the complexes contain cobalt in +3 oxidation state, but $[Co(NH_3)_6]^{3+}$ is diamagnetic while $[CoF_6]^{3-}$ is paramagnetic with magnetic moment 4.90 BM. Explain.

51 Give detailed description of CFT for different types of ligand and explain how CFT explain colour of coordination compound? Use suitable examples to explain.

52 Explain the hybridisation, geometry, magnetic properties, IUPAC nomenclature and comparative stability of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$.

53 Draw all the possible isomers (structural and stereoisomeric) having the composition $[CrBr\,Cl\,(NH_3)_4]$.

54 Square planar complexes of MX_2L_2 type with coordination number of 4 exhibit geometrical isomerism whereas tetrahedral complexes with similar composition do not. Why?

55 (i) Why $[Ni(CN_4)]^{2-}$ form inner orbital complex while $[Ni(H_2O)_6]^{2+}$ form outer orbital complex ?

(ii) Give two significances of coordination compounds.

56 $[Ti(H_2O)_6]^{3+}$ absorbs light of wavelength 500 nm. Name one ligand which would form Ti(III) complex absorbing light of lower wavelength than 500 nm and one ligand which would form a complex absorbing light of wavelength higher than 500 nm.

57 A metal ion M^{n+} having d^4 valence electronic configuration combines with three bidentate ligands to form a complex compound. Assuming $\Delta_o > P$.

(i) Draw the diagram showing d-orbital splitting during this complex formation.

(ii) Write the electronic configuration of the valence electrons of the metal M^{n+} ion in terms of t_{2g} and e_g.

(iii) What type of hybridisation will M^{n+} ion have?

58 Predict the number of unpaired electrons, the magnetic moments for each of the following complex.

(i) $[Fe(CN)_6]^{4-}$

(ii) $[Cr(NH_3)_6]^{2+}$

(iii) $[Sc(H_2O)_6]^{3+}$

LONG ANSWER Type Questions

59 $PtCl_4$ and NH_3 may form five complexes, $A(PtCl_4 \cdot 6NH_3)$, $B(PtCl_4 \cdot 5NH_3)$, $C(PtCl_4 \cdot 4NH_3)$, $D(PtCl_4 \cdot 3NH_3)$ and $E(PtCl_4 \cdot 2NH_3)$. One mole of each A, B, C, D and E reacts with excess of $AgNO_3$ to yield 4, 3, 2 and 1 mole(s) of AgCl respectively, while E gives, no AgCl. The conductance of their solutions are in the order $A > B > C > D > E$. On the basis of Werner's theory, write their structure and give the total number of ions given by one complex.

60 Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers.

(i) $[Co(NH_3)_5NO_3]SO_4$ (ii) $[CoCl(NH_3)_4(H_2O)]Br_2$

(iii) $[Cr(H_2O)_5(SCN)]^{2+}$ (iv) $[Co(en)_3]$ $[Cr(CN)_6]$

(v) $[Pt\ NH_3Cl\ (Py)_2]$

61 (i) What is the basis of formation of the spectrochemical series?

(ii) Draw the structures of geometrical isomers of the following coordination complexes: $[Co(NH_3)_3Cl_3]$ and $[CoCl_2(en)_2]^+$

(en = ethylene diamine and atomic number of Co is 27).

ANSWERS

1 (c) 2 (b) 3 (a) 4 (b)

5 *(a)* When ligands approach a transition metal ion, the *d*-orbitals split into two sets, one with lower energy and other with higher energy. The difference of energy between two sets of orbitals is called CFSE.

6 *(b)* CO can form σ as well as π-bond. Therefore, it is a stronger ligand than $Cl^{\ominus}$.

Or *(b)* CFSE is higher for strong field ligands. So, the correct order is

$$\underset{\text{I}}{[CrCl_6]^{3-}} < \underset{\text{III}}{[Cr(NH_3)_6]^{3+}} < \underset{\text{II}}{[Cr(CN)_6]^{3-}}$$

7 *(d)* The arrangement of ligands in order of their increasing field strengths, i.e. increasing CFSE values is called spectrochemical series.

8 *(c)* $t_{2g}^3 e_g^1$.

9 *(c)* Ionisation isomerism arises when compounds give different ions in the solution, although they have same composition. Only (A) is true.

10 *(a)* Linkage isomerism is shown by the coordination compounds containing ambidentate ligands. Both (A) and (R) are correct and (R) is the correct explanation of (A).

Or The complex $[Pt(NH_3)_4]$ $[PtCl_4]$ shows coordination isomerism. Only (A) is true.

11 *(c)* Only (A) is true.

12 *(c)* Heteroleptic complexes with coordination number 4 and 6 show geometrical isomerism. Only (A) is true.

13 *(b)* Ethane-1, 2-diamine is a neutral ligand as it carries no charge. Oxidation number of Co in the complex ion is +3. Both (A) and (R) are correct but (R) is not the correct explanation of (A).

14 *(a)* Isomers differ in one or more physical or chemical properties because these have different arrangement of atoms. Both (A) and (R) are correct and (R) is correct explanation of (A).

15 *(a)* Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are

same with respect to each other. Both (A) and (R) are correct and R is correct explanation of (A).

16 (*a*) Oxidation number of Cr in $[Cr(NH_3)_3(H_2O)_3]Cl_3$ is same as the charge of the complex ion, i.e. +3 because all the ligands are neutral molecules in this compound. Both (A) and (R) are correct and (R) is correct explanation of (A).

17 (*c*) $[Ni(en)_3]Cl_2$ is more stable than $[Ni(NH_3)_6]Cl_2$, because $[Ni(en)_3]Cl_2$ is a chelating compound which are more stable than complexes with unidentate ligands as the dissociation of complex involves breaking of two bonds instead of one.

$[Ni(en)_3Cl_2]$ show octahedral geometry with d^8 configuration. (A) is correct but (R) is incorrect.

18 (*a*) When a monodentate ligand has two possible donor atoms and attached in two ways to the central metal atom then that ligand is called ambidentate ligand. e.g. nitro (NO_2) and nitrito (ONO). These show linkage isomerism. Both (A) and (R) are correct and (R) is the correct explanation of (A).

19 (*a*) $[Ni(CN)_4]^{2-}$ is square planar and dimagnetic.

$$Ni \rightarrow 3d^8\ 4s^2; \quad Ni^{2+} \rightarrow 3d^8\ 4s^0$$

	3d					4s	4p		
$[Ni(CN)_4]^{2-}$	⥮	⥮	⥮	⥮	xx	xx	xx	xx	

$\underbrace{\qquad\qquad}_{dsp^2\text{-hybridised}}$ square planar

∴ This complex has no unpaired electron.
Both (A) and (R) are correct and (R) is the correct explanation of (A).

20 (*b*) $[Co(en)_2Cl_2]^+$ exist in *cis* and *trans* isomers out of which *cis* isomer will be optically active (*cis-d*-isomer) and (*cis-l*-isomer). Both (A) and (R) are correct but (R) is not the correct explanation of (A).

21 Coordination number of Fe is 6.

22 Pentaamminenitrito-*o*-cobalt (III).

23 Pt (II)

24 Hexochloroplatinate (IV)

25 4 ions

26 Coordination number $4 = [Pt(NH_3)_2Cl_2]$

Coordination number $6 = [Co(NH_3)_4Cl_2]^+$

27 Linkage isomerism.

28 (i) CO (ii) NO^+

29 Using formula $\mu = \sqrt{n(n+2)}$ BM = 1.73 BM

30 Crystal field spliting depends upon the field produced by the ligand and charge on the metal ion.

31 **Hint** Increasing order of field strength.

$$en < CN^- < CO$$

32 **Hint** Greater the charge, greater the stability.

33 Refer to text on page 176.

34 Refer to text on pages 186 and 187.

35 Refer to text on page 176.

36 (i) Refer to text on page 175.
(ii) Refer to text on page 175.

37 Refer to text on page 174.

38 Three isomers.

39 (i) $[Co(NH_3)(Cl)(en)_2]^{2+}$
(ii) $[Ni(H_2O)_2(ox)_2]^{2-}$

40 Refer to text on page 173.

41 Refer to text on pages 196.

42 Refer to text on page 196.

43 Refer to text on page 197.

44 Refer to text on page 185.

45 Refer to text on pages 187.

46 Pentaaquanitrosyl iron (II) oxidation state of Fe = +2

47 Refer to text on pages 183 and 184.

48 Refer to text on pages 183 and 184.

49 (i) Refer to text on page 174.
(ii) Refer to text on page 172.

50 Refer to text on pages 185.

51 Refer to text on pages 186, 187 and 188.

52 Refer to text on pages 185 and 187.

53 Refer to text on page 174 and 175.

54 Refer to text on pages 175 and 176.

55 (i) Refer to text on page 184.
(ii) Refer to text on page 197.

56 Refer to text on page 187 and 188.

57 Refer to text on pages 186 and 187.

58 Refer to text on pages 185.
(iii) **[Hint]** $[Sc(H_2O)_6]^{3+}$ = diamagnetic.

59 Refer to text on page 170.

60 Refer to text on pages 174 and 175.

61 (i) Refer to text on page 187.
(ii) Refer to text on pages 174 and 175.

06

HALOALKANES AND HALOARENES

Halogens, being among the most electronegative elements, have great tendency to form various derivatives of organic compounds. These derivatives are of great importance in terms of day-to-day applications, synthesis of other useful compounds, chemical research, etc. They can be synthesised in laboratories and are also found in nature.

These compounds persist in the environment due to their resistance to breakdown by soil bacteria. They have great importance in medicines as well as in healthcare, e.g. chlorine containing antibiotic, chloramphenicol produced by soil microorganisms is effective in treatment of typhoid fever. Even our body produces iodine containing hormone, thyroxine, the deficiency of which causes a disease called goitre. These halogenated compounds involve haloalkanes and haloarenes which are discussed in this chapter.

Synthetic halogen compounds, e.g. chloroquine is used in the treatment of malaria and halothane ($CF_3CHClBr$) is used as an anaesthetic in surgery. In this unit, we will study the important methods of preparation, physical and chemical properties and uses of organohalogen compounds.

CHAPTER CHECKLIST

- Classification, Nomenclature and Nature of Haloalkanes and Haloarenes
- Methods of Preparation of Haloalkanes and Haloarenes
- Properties of Haloalkanes and Haloarenes
- Polyhalogen Compounds

TOPIC 1

Classification, Nomenclature and Nature of Haloalkanes and Haloarenes

The replacement of hydrogen atom(s) from a hydrocarbon, aliphatic or aromatic, by halogen atom(s) (i.e. F, Cl, Br, I) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

Haloalkanes contain halogen atom(s) attached to the sp^3-hybridised carbon atom(s) of an alkyl group, whereas haloarenes contain halogen atom(s) attached to sp^2-hybridised carbon atom(s) of an aryl group.

CLASSIFICATION

Haloalkanes and haloarenes may be classified as follows:

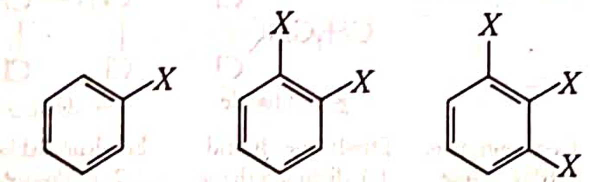
1. On the Basis of Number of Halogen Atoms

Depending on the number of halogen atoms in their structures, haloalkanes and haloarenes may be mono, di, tri or polyhalogen (tetra, penta, etc.) compounds.

CH_3X or C_2H_5X — Monohaloalkane

CH_2X-CH_2X — Dihaloalkane

$CH_2X-CHX-CH_2X$ — Trihaloalkane



Monohaloarene Dihaloarene Trihaloarene

(where, X = F, Cl, Br, I)

2. On the Basis of Nature of Carbon of C—X Bond

Monohalo compounds may further be classified according to the hybridisation of the carbon atom to which halogen is bonded, as discussed below.

A. Compounds Containing sp^3 C—X Bond

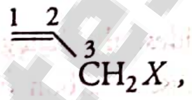
These are classified into three types:

(i) **Alkyl halides or Haloalkanes (R—X)** In these halides, the halogen atom (X) is bonded to an alkyl group (R). They form a homologous series of compounds represented by the formula $C_nH_{2n+1}X$. They are further classified as primary (1°), secondary (2°) or tertiary (3°) depending upon the nature of carbon atom to which the halogen is attached.

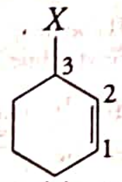
e.g. $R'-CH_2-X$ Primary (1°); $R''-CHR'-X$ Secondary (2°); $R''-CR'R'''-X$ Tertiary (3°)

CH_3-CH_2-Br Bromoethane (Primary or 1°); $H-C(CH_3)_2-Br$ 2-bromopropane (Secondary or 2°); $CH_3-C(CH_3)_2-Br$ 2-bromo-2-methylpropane (Tertiary or 3°)

(ii) **Allylic halides** In these halides, the halogen is bonded to the sp^3-hybridised carbon atom next to carbon-carbon double bond which is also called allylic carbon. Hence, these halides are called allylic halides.

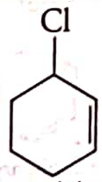
e.g. 

3-haloprop-1-ene (Allyl halide)



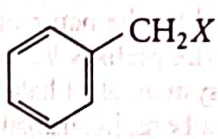
3-halocyclohex-1-ene

$CH_2{=}CH-CH_2-Cl$, 3-chloroprop-1-ene

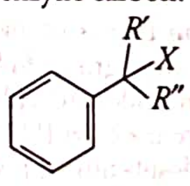


3-chlorocyclohex-1-ene

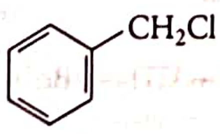
(iii) **Benzylic halides** In these halides, the halogen atom is bonded to the sp^3-hybridised carbon atom next to an aromatic ring, i.e. to a benzylic carbon.

e.g. 

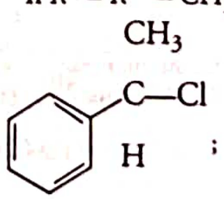
(1°)



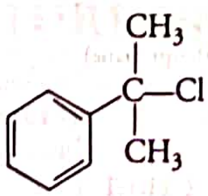
[If $R' = CH_3$, $R'' = H$ (2°)
If $R' = R'' = CH_3$ (3°)]



(1°)



(2°)



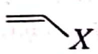
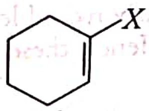
(3°)

B. Compounds Containing $sp^2C—X$ Bond

In these compounds, halogen is directly attached to one of the doubly bonded carbon atom $(—\overset{|}{C}=\overset{|}{C}—X)$.

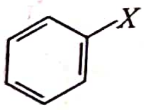
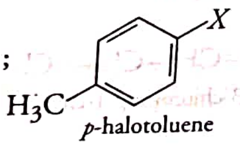
These are classified into the following two types:

(i) **Vinylic halides** In these halides, the halogen atom is bonded to the sp^2-hybridised carbon of one of the carbon atoms of a double bond, i.e. vinylic carbon.

e.g.  ; 

Haloethene (Vinyl halide) 1-halocyclohex-1-ene

(ii) **Aryl halides** In these halides, the halogen atom is bonded to the sp^2-hybridised carbon atom of an aromatic ring.

e.g.  ; 

Halobenzene *p*-halotoluene

NOMENCLATURE

1. For Monosubstituted Haloalkane

The **common names** of alkyl halides are derived by naming the alkyl group followed by the name of halide (chloride, bromide, etc). Here, the prefixes *n*-, *iso*-, *sec*-, *tert*-, etc., are used. In IUPAC system, alkyl halides are named as halosubstituted hydrocarbons, i.e. haloalkanes. The names are written by prefixing the word 'halo' to the name of alkane corresponding to the longest continuous carbon chain having the halogen atom.

e.g. $CH_3CH_2CH_2I$;

Common name *n*-propyl iodide
IUPAC name (1-iodopropane)

$$CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_2—Br;$$

Common name *iso*-butyl bromide
IUPAC name (1-bromo-2-methylpropane)

$$CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2Cl$$

Common name *neo*-pentyl chloride
IUPAC name (1-chloro-2, 2-dimethylpropane)

2. For Disubstituted Haloalkane

The dihaloalkanes having the same type of halogen atoms are named as alkylidene or alkylene dihalides. The dihalo compounds having same type of halogen atoms are further classified as:

(i) *Geminal* **halides** Here halogen atoms are present on the same carbon atom.

(ii) *Vicinal* **halides** Here halogen atoms are present on the adjacent carbon atoms.

In common name system, *gem*-dihalides are named as alkylidene halides, whereas *vic*-dihalides are named as alkylene dihalides. In IUPAC system, they are named as dihaloalkanes.

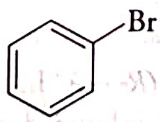
e.g. $CH_3CH\begin{matrix} Cl \\ Cl \end{matrix}$; $\underset{Cl}{\underset{|}{CH_2}}—\underset{Cl}{\underset{|}{CH_2}}$

	gem-dihalide	*vic*-dihalide
Common name	Ethylidene chloride	Ethylene dichloride
IUPAC name	1,1-dichloroethane	1,2-dichloroethane

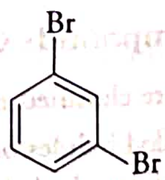
3. For Haloarenes

They are named by prefixing 'halo' before the name of the aromatic hydrocarbon.

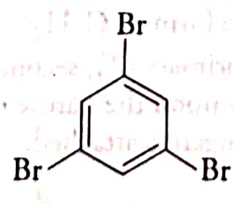
Haloarenes are the common as well as IUPAC names of aryl halides. For dihalogen derivatives, the prefixes *o*-, *m*-, *p*- are used in common system but in IUPAC system, the numerals 1,2; 1,3 and 1,4 are used respectively.



(a)



(b)

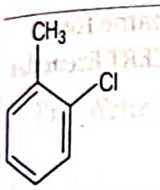
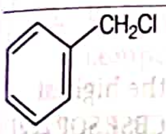


(c)

Common and IUPAC names of above figures are given below:

	Common name	IUPAC name
(a)	Bromobenzene	Bromobenzene
(b)	*m*-dibromobenzene	1,3-dibromobenzene
(c)	*sym*-tribromobenzene	1,3,5-tribromobenzene

Common and IUPAC names of some halides

Structure	Common name	IUPAC name
$CH_3CH_2CH_2F$	*n*-propyl fluoride	1-fluoropropane
$(CH_3)_3CCH_2—Br$	*neo*-pentyl bromide	1-bromo-2,2-dimethyl propane
$CH_3CH_2CH(Cl)CH_3$	*sec*-butyl chloride	2-chlorobutane
$(CH_3)_3C—Br$	*tert*-butyl bromide	2-bromo-2-methyl propane
$CH_2=CH—CH_2Br$	Allyl bromide	3-bromopropene
$CH_2=CHCl$	Vinyl chloride	Chloroethene
CH_2Cl_2	Methylene chloride	Dichloromethane
$CHCl_3$	Chloroform	Trichloromethane
$CHBr_3$	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
	*o*-chlorotoluene	1-chloro-2-methyl benzene or 2-chlorotoluene
	Benzyl chloride	Chlorophenylmethane

EXAMPLE |1| Write the IUPAC names of the following compounds:

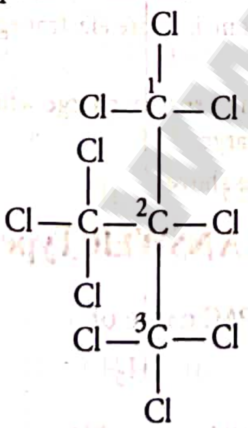
(i) $(CCl_3)_3CCl$

(ii) $(CH_3)_3CCH=C(Cl)C_6H_4I$-*p* **NCERT**

Sol.

(i) We follow the following steps:

I. To write the IUPAC name, we first expand the structure of the compound as follows:

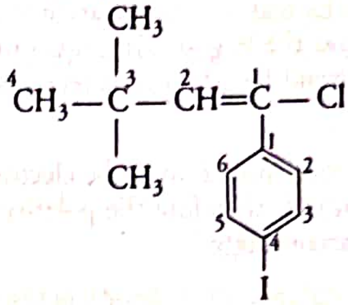


II. Now we do the numbering of the carbon chain, specifically from the end where functional group is nearer and/or more in number. In this case, numbering from both the ends is equivalent.

III. Then we write the IUPAC name, counting the functional groups and their positions.

Thus, the name of the given structure is 2-(trichloromethyl)-1,1,1,2,3,3,3,-heptachloropropane.

(ii) The expanded structure is:



In case, if a halogen (functional group) is attached to a benzene ring which in turn, is attached to an alkane or alkene then the position of that halogen will be written in bracket as

1-chloro-1-(4-iodophenyl)-3,3-dimethylbut-1-ene.

ISOMERISM

Haloalkanes exhibit the following two types of isomerism:

Chain Isomerism

If a haloalkane has four or more carbon atoms, it can exhibit chain isomerism by making a branched or straight chain compound. e.g. Butyl bromide has two possible chain isomers as follows:

$$CH_3—CH_2—CH_2—CH_2—Br,$$
1-bromobutane

$$CH_3—\underset{}{\overset{CH_3}{\overset{|}{CH}}}—CH_2Br$$
1-bromo-2-methylpropane

Positional Isomerism

A haloalkane having atleast three carbon atoms show position isomerism by having halogen atoms at different carbon number, in a chain, in different isomers.

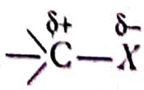
e.g. Propyl bromide exhibits two position isomers as follows:

$$CH_3CH_2CH_2Br\ ; \quad CH_3—\overset{Br}{\overset{|}{CH}}—CH_3$$
1-bromopropane ; 2-bromopropane

NATURE OF C—*X* BOND

Electronegativity of halogen atom is greater than that of carbon atom due to which the shared pair of electron in C—*X* bond lies closer to the halogen atom.

As a result, the halogen atom bears a partial negative charge whereas, the carbon atom bears a partial positive charge.



As we go down in a group of the periodic table, the size of halogen atom increases, fluorine atom is the smallest and iodine atom is the largest. Consequently, the carbon-halogen bond length also increases from C—F to C—I.

Further, as we move from F to I, the electronegativity of the halogen decreases, therefore the polarity of the C—*X* bond decreases accordingly.

Carbon-halogen (C–*X*) bond lengths, bond enthalpies and dipole moments

Bond between carbon and halogen	Bond length/pm	C—*X* Bond enthalpies / kJ mol^{-1}	Dipole moment/Debye
CH_3-F	139	452	1.847
CH_3-Cl	178	351	1.860
CH_3-Br	193	293	1.830
CH_3-I	214	234	1.636

In haloarenes, sp^2 hybridised carbon of benzene is bonded to halogen and C—*X* bond is also polar as in haloalkanes due to higher electronegativity of halogen. Apart from this, lone pair of electrons of halogen atom are involved in resonance with benzene ring. So, this C—*X* bond acquires partial double bond character.

The C—*X* bond of haloarenes is less polar than C—*X* bond of haloalkanes. This is supported by the fact that dipole moment of chlorobenzene ($\mu = 1.69$ D) is little lower than that of CH_3Cl ($\mu = 1.83$ D). The C—*X* bond of a haloarene is usually shorter than haloalkane.

The reason for this occurrence is that haloarenes are more electron rich, due to the presence of double bonds, than haloalkanes and the benzene ring as a whole due to resonance is strongly attracted towards electronegative halogen atoms.

TOPIC PRACTICE 1

OBJECTIVE Type Questions

1. The position of Br in the compound $CH_3CH=CHC(Br)(CH_3)_2$ can be classified as .... **NCERT Exemplar**

(a) allyl (b) aryl
(c) vinyl (d) secondary

2. Ethylidene chloride is a/an .... **NCERT Exemplar**

(a) *vic*-dihalide
(b) *gem*-dihalide
(c) allylic halide
(d) vinylic halide

3. Alkenes decolourise bromine water in presence of CCl_4 due to formation of **CBSE SQP (Term I)**

(a) allyl bromide (b) vinyl bromide
(c) bromoform (d) *vicinal* dibromide

4. Which is the correct IUPAC name for **NCERT Exemplar**

$$\begin{array}{l} CH_3-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2-Br\ ? \end{array}$$

(a) 1-bromo-2-ethylpropane
(b) 1-bromo-2-ethyl-2-methylethane
(c) 1-bromo-2-methylbutane
(d) 2-methyl-1-bromobutane

5. What should be the correct IUPAC name for diethylbromomethane? **NCERT Exemplar**

(a) 1-bromo-1, 1-diethylmethane
(b) 3-bromopentane
(c) 1-bromo-1-ethylpropane
(d) 1-bromopentane

6. Which of the following isomer has the highest melting point? **CBSE SQP 2021**

(a) 1, 2-dichlorobenzene
(b) 1, 3 -dichlorobenzene
(c) 1, 4-dichlorobenzene
(d) All isomers have same melting points

7. Possible number of isomers of $C_3H_6Cl_2$ compound are

(a) 2 (b) 4 (c) 6 (d) 8

8. Carbon-halogen bond is polarised because

(a) halogen atom is less electronegative
(b) halogen atom is more electronegative than carbon atom
(c) carbon bears negative charge while halogen bears positive charge
(d) None of the above

VERY SHORT ANSWER Type Questions

9. Write the IUPAC name of

$$CH_3CH=CH-\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3\ .$$

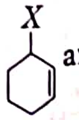
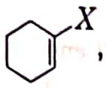
Delhi 2013

10. Write the IUPAC name of the following compound.

$$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-CH=CH_2$$

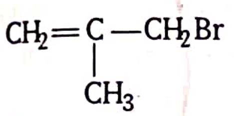
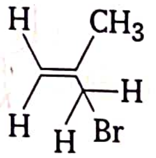
Delhi 2013

11. Write the structure of 2, 4-dinitrochlorobenzene. **Delhi 2017**

12. Out of  and , which is an example of allylic halide? **All India 2017**

13. Write the structure of 3-bromo-2-methylprop-1-ene. **Delhi 2017**

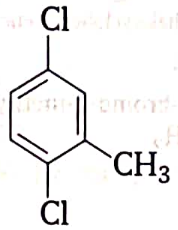
14. Give the IUPAC name of the following compound.

 *Or* 

All India 2010; Foreign; Delhi 2012

15. Write the IUPAC name of $(CH_3)_2CH \cdot CH(Cl)CH_3$. **Delhi 2014**

16. Write the IUPAC name of the following compound.

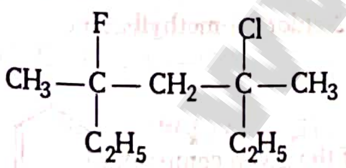


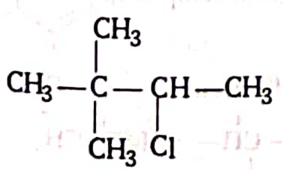
All India 2013

17. Write the structure of the compound 4-*tert*-butyl-3-iodoheptane. **NCERT Intext; NCERT; All India 2010 C**

SHORT ANSWER Type I Questions

18. Write the IUPAC name of the following compounds.

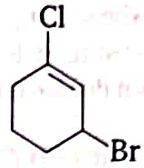
(i) 

(ii) 

All India 2013

19. Give the IUPAC names of the following compounds.
   (i) $CH_3CH(Cl)CH(Br)CH_3$
   (ii) $CHF_2CBrClF$
   (iii) $ClCH_2C \equiv CCH_2Br$
   (iv) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$ **NCERT**

20. Write the IUPAC name of the compound shown alongside and mention the hybridisation of each carbon-halogen bond.



21. Draw the structure of the following compounds.
   (i) 2,2-dimethyl-1-bromobutane
   (ii) 2,2,4,4-tetramethylhexane

22. Write the structures of the following organic halogen compounds.
   (i) 1-bromo-4-*sec*-butyl-2-methylbenzene
   (ii) 1, 4-dibromobut-2-ene

NCERT Intext; All India 2011C, 2010 C; Delhi 2011 C

23. Write the structures of different dihalogen derivatives of propane. **NCERT Intext**

24. Write the isomers of the compound having formula, C_4H_9Br. **NCERT**

SHORT ANSWER Type II Questions

25. Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides.
   (i) $(CH_3)_2CHCH(Cl)CH_3$
   (ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$
   (iii) $CH_3CH_2C(CH_3)_2CH_2I$
   (iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$
   (v) $CH_3CH(CH_3)CH(Br)CH_3$
   (vi) $CH_3C(C_2H_5)_2CH_2Br$ **NCERT**

26. Write the structures of the following organic halogen compounds.
   (i) *p*-bromochlorobenzene
   (ii) 2-(2-chlorophenyl)-1-iodooctane
   (iii) 2-bromobutane **NCERT**

27. Name the following halides according to the IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides.
   (i) $CH_3C(Cl)(C_2H_5)CH_2CH_3$
   (ii) $CH_3CH{=}C(Cl)CH_2CH(CH_3)_2$
   (iii) $CH_3CH{=}CHC(Br)(CH_3)_2$
   (iv) $p\text{-}ClC_6H_4CH_2CH(CH_3)_2$
   (v) $m\text{-}ClCH_2C_6H_4CH_2C(CH_3)_3$
   (vi) $o\text{-}Br{-}C_6H_4CH(CH_3)CH_2CH_3$ **NCERT**

HINTS AND EXPLANATIONS

1. (a) Allyl halides are those compounds in which the halogen atom is bonded to sp^3hybridised carbon atom next to carbon-carbon double bond.
e.g.,
$CH_2 = CH — CH_2X$ and $CH_3CH = CHC(Br)(CH_3)_2$.

2. (b) In *gem*-dihalides, two halogen atoms are present on the same carbon atom. They are known as alkylidene halides.

$$CH_3CH\begin{matrix}\diagup Cl \\ \diagdown Cl\end{matrix}$$

Common name Ethylidene chloride
IUPAC name 1, 1-dichloroethane

3. (d) Bromine in CCl_4 is a test for unsaturation in hydrocarbons. Alkene and alkynes contain double and triple bond respectively and thus decolorises the red coloured bromine solution vicinal dibromide takes part in saturation process.

$$CH_2{=}CH_2 + Br_2 \longrightarrow BrCH_2{—}CH_2Br$$

Hence, option (d) is correct.

4. (c) The correct IUPAC name of the given compound is

$$CH_3 — \overset{2}{C}H — \overset{1}{C}H_2 — Br$$
$$\quad\quad\ |$$
$$\quad\quad\ {}^{3}CH_2$$
$$\quad\quad\ |$$
$$\quad\quad\ \underset{4}{CH_3}$$

1-bromo-2-methylbutane

5. (b) Structure of the diethylbromomethane is given below

$$\underset{5}{H_3C} — \underset{4}{H_2C} — \underset{3}{\overset{Br}{\overset{|}{HC}}} — \underset{2}{CH_2} — \underset{1}{CH_3}$$

So, the IUPAC name is 3-bromopentane.

6. (c) The melting point is based on the strength of the lattice strucure of a compound. *Para*-isomer has a higher melting point in comparison to *ortho*-isomer and *meta*-isomer of the same compound. It is because *para*-isomer are symmetric and have compact crystal lattice in comparison to ortho-isomer and meta-isomer.

7. (b) Possible isomers of $C_3H_6Cl_2$ compound are

(i) $\underset{Cl}{\underset{|}{CH_2}}\ \underset{Cl}{\underset{|}{CH}}CH_3$
1, 2-dichloropropane

(ii) $CH_2ClCH_2CH_2Cl$
1,3-dichloropropane

(iii) $CHCl_2CH_2CH_3$
1,1-dichloropropane

(iv) $CH_3CCl_2CH_3$
2, 2-dichloropropane

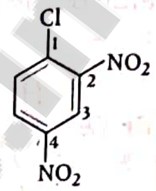
8. (b) Since, halogen atom is more electronegative than carbon atom, carbon-halogen bond ($C—X$) gets polarised.

9. 4-bromo-4-methylpent-2-ene

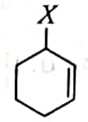
10. $\overset{5}{C}H_3 — \underset{Cl}{\underset{|}{\overset{4}{C}H}} — \overset{3}{C}H_2 — \overset{2}{C}H = \overset{1}{C}H_2$

4-chloropent-1-ene

11. The structure of 2,4-dinitrochlorobenzene is



12. In allylic halides, the halogen is bonded to the sp^3-hybridised carbon atom next to a carbon-carbon double bond. Thus,



3-halocyclohex-1-ene

is an allylic halide.

13. The structure of 3-bromo-2-methylprop-1-ene is

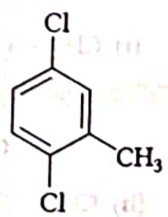
$$BrCH_2 — \underset{CH_3}{\underset{|}{C}} = CH_2$$

14. $\overset{1}{C}H_2 = \underset{CH_3}{\underset{|}{\overset{2}{C}}} — \overset{3}{C}H_2Br$

IUPAC Name : 3-bromo-2-methylprop-1-ene

15. $\begin{matrix}H_3C \diagdown \\ \underset{4}{H_3C} \diagup\end{matrix} \underset{3}{CH} — \underset{2}{\overset{Cl}{\overset{|}{CH}}} — \underset{1}{CH_3}$

IUPAC Name : 2-chloro-3-methylbutane

16. IUPAC name of the given compound  is

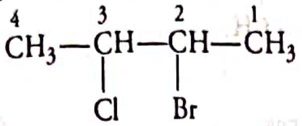
1,4-dichloro-2-methylbenzene

17. $\overset{1}{C}H_3 — \overset{2}{C}H_2 — \underset{I}{\underset{|}{\overset{3}{C}H}} — \overset{4}{C}H — \overset{5}{C}H_2\overset{6}{C}H_2\overset{7}{C}H_3$

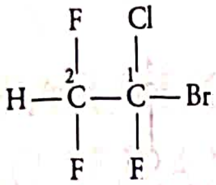
$$H_3C — \underset{CH_3}{\underset{|}{\overset{|}{C}}} — CH_3$$

18. (i) 3-chloro-5-fluoro-3,5-dimethylheptane
(ii) 2-chloro-3,3-dimethylbutane (halogen is preferred over alkyl group while naming).

19. To write the IUPAC name, draw the structures, find the longest carbon chain, give the numbers and name them.

(i) 

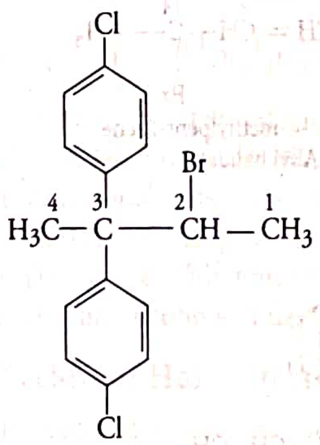
IUPAC Name : 2-bromo-3-chlorobutane

(ii) 

IUPAC Name : 1-bromo-1-chloro-1,2,2-trifluoroethane

(iii) $\overset{4}{Cl—CH_2}—\overset{3}{C}\equiv\overset{2}{C}—\overset{1}{CH_2}—Br$

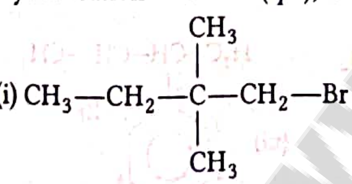
IUPAC Name : 1-bromo-4-chlorobut-2-yne

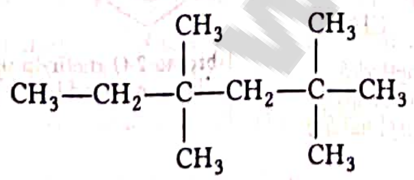
(iv) 

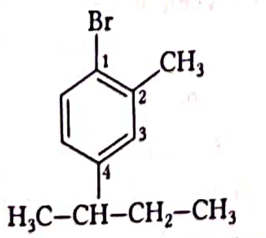
IUPAC Name : 2-bromo-3,3-*bis* - (4-chlorophenyl)butane

20. IUPAC Name : 3-bromo-1-chlorocyclohex-1-ene

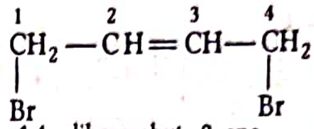
Hybridisation C—Cl (sp^2), C—Br (sp^3)

21. (i) 

(ii) 

22. (i) 

1-bromo-4-sec-butyl-2-methylbenzene

(ii) 

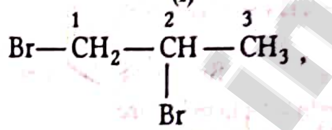
1,4 - dibromobut - 2 - ene

23. The structures of different dihalogen derivatives of propane are :

(i) $Br—\overset{1}{CH_2}—\overset{2}{CH_2}—\overset{3}{CH_2}—Br$

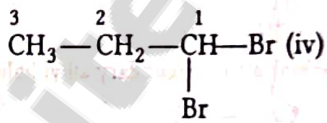
1, 3 - dibromopropane

(I)

(ii) 

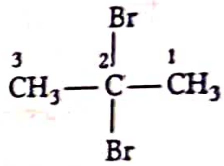
1, 2-dibromopropane

(II)

(iii) 

1, 1 - dibromopropane

(III)

(iv) 

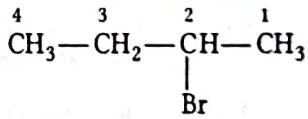
2, 2 - dibromopropane

(IV)

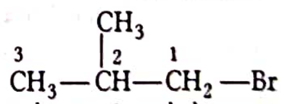
24. It has four isomers (two positional isomers and two chain isomers).

(i) $\overset{4}{CH_3}—\overset{3}{CH_2}—\overset{2}{CH_2}—\overset{1}{CH_2}Br$

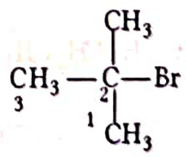
1 - bromobutane

(ii) 

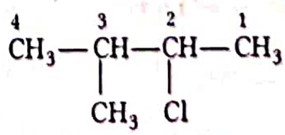
2 -bromobutane

(iii) 

1- bromo -2-methylpropane

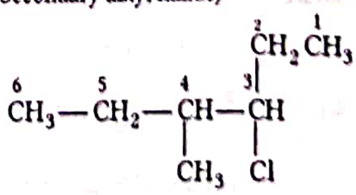
(iv) 

2-bromo-2-methylpropane

25. (i) 

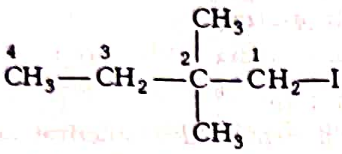
2-chloro -3-methylbutane

(Secondary alkyl halide)

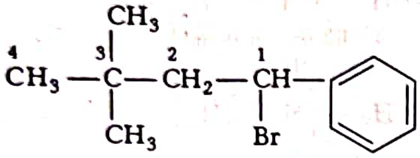
(ii) 

3-chloro-4-methylhexane

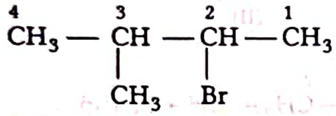
(Secondary alkyl halide)

(iii) 

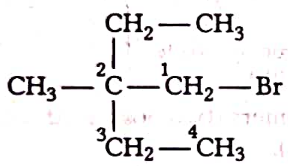
1-iodo -2,2-dimethylbutane
(Primary alkyl halide)

(iv) 

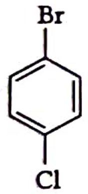
1-bromo-3,3-dimethyl -1-phenylbutane
(Secondary benzyl halide)

(v) 

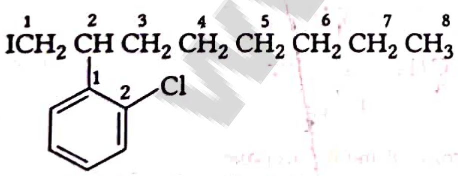
2 - bromo - 3 -methylbutane (Secondary alkyl halide)

(vi) 

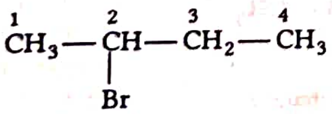
1-bromo-2-ethyl-2-methylbutane
(Primary alkyl halide)

26. (i) 

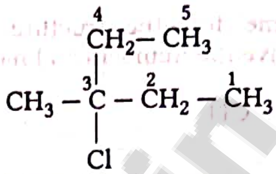
p-bromochlorobenzene

(ii) 

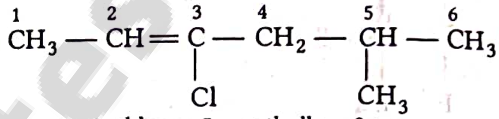
2-(2-chlorophenyl)-1-iodooctane

(iii) 

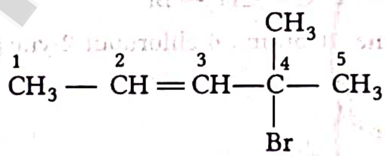
2-bromobutane

27. (i) 

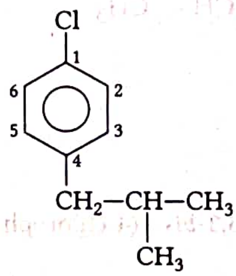
3-chloro-3-methylpentane
(Tertiary alkyl halide)

(ii) 

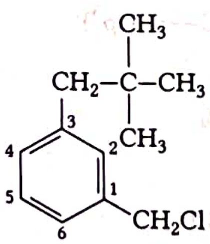
3-chloro - 5 - methylhex-2-ene
(Vinyl halide)

(iii) 

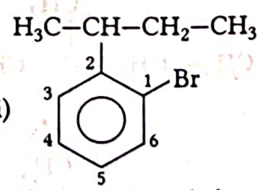
4- bromo -4-methylpent-2-ene
(Allyl halide)

(iv) 

1-chloro-4-(2-methylpropyl) benzene
(Aryl halide)

(v) 

1-chloromethyl-3
(2, 2-dimethylpropyl)
benzene (Benzyl halide)

(vi) 

1-bromo-2-(1-methylpropyl)
benzene (Aryl halide)

|TOPIC 2|
Methods of Preparation of Haloalkanes and Haloarenes

PREPARATION OF HALOALKANES

Haloalkanes can be prepared from wide range of organic compounds through various methods. Some important methods of preparation are discussed below:

Preparation from Alcohols

This is the most convenient method for the preparation of haloalkanes in the laboratory. In this method, the hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides or thionyl chloride. Different reagents can be used to get haloalkanes from alcohols as described below:

(a) By the Action of Halogen Acids

Haloalkanes are prepared by the treatment of alcohols with halogen acids as follows:

$$\underset{\text{Alcohol}}{ROH} + \underset{\text{Halogen acid}}{HX} \longrightarrow \underset{\text{Haloalkane}}{RX} + \underset{\text{Water}}{H_2O}$$

The rate of reaction depends on the nature of alcohol as well as the halogen acid.

(i) The reaction of primary (1°) and secondary (2°) alcohols with halogen acids require the presence of a catalyst, $ZnCl_2$ which acts as a Lewis acid and helps in the cleavage of C—O bond. Chloroalkanes are prepared by the action of hydrochloric acid to the primary and secondary alcohols in the presence of anhydrous zinc chloride **(Groove's process)**.

$$\underset{\text{Ethyl alcohol (1°)}}{CH_3CH_2OH} + HCl(g) \xrightarrow{\text{Anhydrous } ZnCl_2} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + H_2O$$

$$\underset{\textit{iso}\text{-propyl alcohol (2°)}}{\begin{array}{c} CH_3 \\ | \\ CH_3-C-OH \\ | \\ H \end{array}} + HCl(g) \xrightarrow{\text{Anhydrous } ZnCl_2} \underset{\textit{iso}\text{-propyl chloride}}{\begin{array}{c} CH_3 \\ | \\ CH_3-C-Cl \\ | \\ H \end{array}} + H_2O$$

Tertiary alcohols are very reactive and therefore, their reactions are conducted by simply shaking with concentrated HCl at room temperature even in the absence of zinc chloride.

$$\underset{\textit{tert}\text{-butyl alcohol}}{\begin{array}{c} CH_3 \\ | \\ CH_3-C-OH \\ | \\ CH_3 \end{array}} + HCl\,(\text{conc.}) \xrightarrow{\text{Room temperature}} \underset{\substack{\textit{tert}\text{-butyl chloride} \\ \text{(2-chloro-2-methylpropane)}}}{\begin{array}{c} CH_3 \\ | \\ CH_3-C-Cl \\ | \\ CH_3 \end{array}} + H_2O$$

(ii) Bromoalkanes are prepared by heating an alcohol with constant boiling of HBr (48%) in the presence of conc. H_2SO_4, which acts as a catalyst.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + HBr \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} + H_2O$$

HBr can also be generated *in situ* by the action of conc. H_2SO_4 on KBr or NaBr.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + KBr + H_2SO_4 \xrightarrow{\Delta} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} + KHSO_4 + H_2O$$

(iii) Iodoalkanes are prepared by heating an alcohol with constant boiling HI (57%).

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + HI \xrightarrow{\text{Reflux}} \underset{\text{Iodoethane}}{CH_3CH_2I} + H_2O$$

HI can also be generated *in situ* by the action of 95% phosphoric acid on KI.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + KI + \underset{\substack{\text{Phosphoric} \\ \text{acid}}}{H_3PO_4} \xrightarrow{\Delta} \underset{\text{Iodoethane}}{CH_3CH_2I} + KH_2PO_4 + H_2O$$

This reaction gives good yields of alkyl iodides.

Note

(i) Secondary and tertiary bromides and iodides cannot be prepared from their respective alcohols in the presence of conc. H_2SO_4 as they undergo dehydration to form alkenes.

(ii) The order of reactivity of alcohols with a given haloacid is 3° > 2° > 1°.

(iii) The order of reactivity of halogen acids with alcohols is HI > HBr > HCl.

(b) By the Action of Phosphorus Halides

(i) Chloroalkanes are obtained by the action of PCl_5 or PCl_3 on alcohols.

$$R—OH + PCl_5 \longrightarrow R—Cl + POCl_3 + HCl$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + PCl_5 \longrightarrow \underset{\text{Chloroethane}}{CH_3CH_2Cl} + \underset{\text{Phosphoryl chloride}}{POCl_3} + HCl$$

$$\underset{\text{Ethyl alcohol}}{3CH_3CH_2OH} + PCl_3 \longrightarrow \underset{\text{Chloroethane}}{3CH_3CH_2Cl} + \underset{\text{Phosphorous acid}}{H_3PO_3}$$

(ii) Bromoalkanes and iodoalkanes are prepared by the reaction of PBr_3 and PI_3, respectively with the alcohols. PBr_3 and PI_3 are usually generated *in situ* by the reaction of red phosphorus with bromine and iodine, respectively.

$$R—OH \xrightarrow{\text{Red P}/X_2} R—X \text{ (where, } X = \text{Br, I)}$$

$$CH_3—OH \xrightarrow{\text{Red P}/Br_2} CH_3—Br$$

(c) By the Action of Thionyl Chloride

Chloroalkanes are prepared by refluxing the alcohols with $SOCl_2$ in the presence of pyridine.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{Chloroethane}}{CH_3CH_2Cl} + SO_2\uparrow + HCl\uparrow$$

This method is usually preferred since both the products of this reaction (SO_2 and HCl) are escapable gases. Hence, the reaction gives pure alkyl halide.

Note The above three methods are not applicable for the preparation of aryl halides because the C—O bond in phenol has a partial double bond character and is difficult to break being stronger than a single bond.

Preparation from Hydrocarbons

Alkyl halides can be prepared from alkanes through substitution and from alkenes through addition of halogen acids or through allylic substitution.

(a) By Free Radical Halogenation

Alkanes react with halogens (Cl_2 and Br_2) in the presence of UV light to form haloalkanes. The reaction proceeds through free radical mechanism and gives a complex mixture of isomeric mono and polyhaloalkanes which are difficult to separate as pure compounds.

e.g. $$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or Heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3\underset{\underset{Cl}{|}}{C}HCH_2CH_3$$

The relative amounts of these isomeric haloalkanes depend upon the nature of the halogen and the number and type of hydrogen atoms (1°, 2° and 3°) which are being substituted. For the ease of substitution, various hydrogens follows the sequence as:

$$3° > 2° > 1°$$

(b) From Alkenes

(i) Addition of Hydrogen Halides

By the reaction with hydrogen halide, an alkene is converted to the corresponding alkyl halide.

e.g. $$\underset{\text{Alkene}}{>C{=}C<} + HX \longrightarrow \underset{\text{Haloalkane}}{—\underset{\underset{H}{|}}{\overset{|}{C}}—\underset{\underset{X}{|}}{\overset{|}{C}}—}$$

The decreasing order of reactivity of the halogen acids is

$$HI > HBr > HCl > HF$$

In case of addition to symmetrical alkenes, only one addition product is formed.

But in case of addition to unsymmetrical alkenes, Markovnikov's rule is followed, e.g. propene yields two products but only one predominates according to Markovnikov's rule.

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + HI \longrightarrow \underset{\substack{\text{1-iodopropane}\\\text{(Minor)}}}{CH_3CH_2CH_2I} + \underset{\substack{\text{2-iodopropane}\\\text{(Major)}}}{CH_3—\underset{\underset{I}{|}}{C}H—CH_3}$$

However, in the presence of a peroxide, the addition of HBr to an unsymmetrical alkene, proceeds in contrary to the Markovnikov's rule. This effect is known as Kharasch effect or peroxide effect.

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{\text{1-bromopropane}}{CH_3CH_2CH_2Br}$$

It is informally called as anti-Markovnikov's addition.

(ii) Addition of Halogens

In the laboratory, addition of bromine (Br_2) to an alkene in CCl_4 results in discharge of reddish-brown colour of bromine constitutes an important method for the detection of double bond in a molecule. The addition results in the synthesis of *vic*-dibromides which are colourless.

On adding Br_2 or Cl_2 to alkenes, the addition occurs at the double bond forming *vic*-dihalides.

e.g. $$\underset{\text{Alkene}}{H_2C=CH_2} + Br_2 \xrightarrow{CCl_4} \underset{\textit{vic}\text{-dibromide}}{BrCH_2CH_2Br}$$

Preparation by Halogen Exchange

Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with NaI in dry acetone. This reaction is known as Finkelstein reaction.

$$R—X + NaI \longrightarrow R—I + NaX \quad [X = Cl, Br]$$

e.g. $$CH_3CH_2Br + NaI \xrightarrow[\Delta]{\text{Acetone}} CH_3CH_2I + NaBr$$

NaBr or NaCl, thus formed gets precipitated in dry acetone which facilitates the forward reaction according to Le-Chatelier's principle. Fluoroalkanes are best prepared by treating alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3. This reaction is known as Swarts reaction.

$$\underset{\text{Methyl bromide}}{CH_3Br} + \underset{\text{Silver fluoride}}{AgF} \longrightarrow \underset{\text{Fluoromethane}}{CH_3F} + AgBr$$

Preparation from Silver Salts of Acids

Generally, bromoalkanes are prepared by refluxing the silver salts of acids with bromine in CCl_4. This reaction is known as Borodine-Hunsdiecker reaction. The reaction can be depicted as:

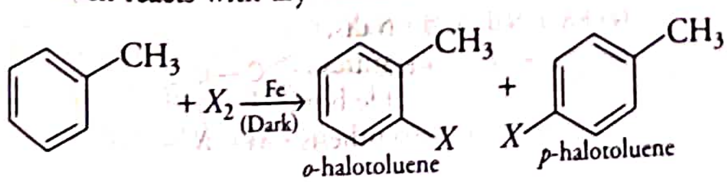
$$CH_3CO\bar{O}\overset{+}{A}g + Br_2 \xrightarrow{CCl_4} \underset{\text{Methyl bromide}}{CH_3Br} + CO_2\uparrow + AgBr$$

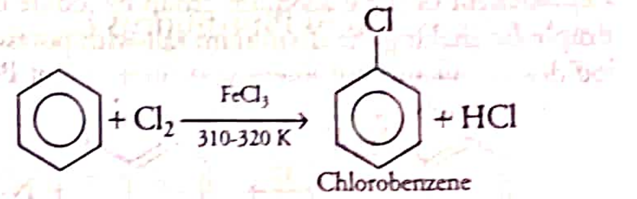
PREPARATION OF HALOARENES

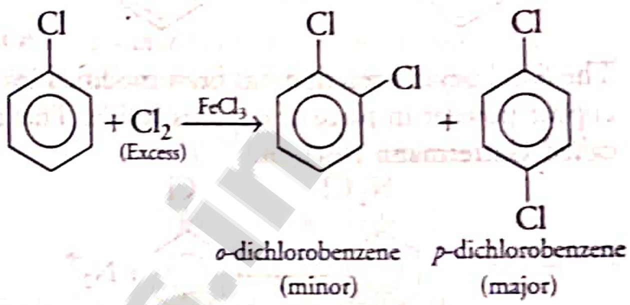
Haloarenes can be prepared by the following methods:

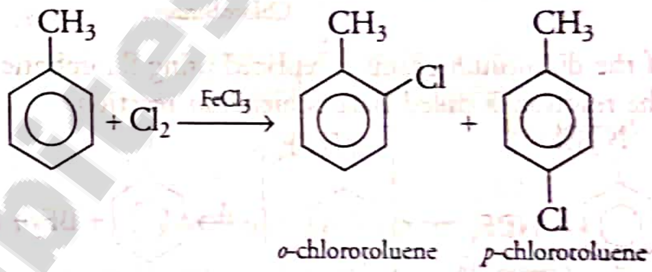
By Electrophilic Substitution of Aromatic Hydrocarbons

Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine, respectively in dark, at ordinary temperature in the presence of a Lewis acid catalysts such as iron or ferric halides or aluminium halides ($FeCl_3$, $FeBr_3$, $AlCl_3$). Lewis acid is used to generate the electrophile, i.e. Cl^+ and Br^+ which reacts with aryl halide.





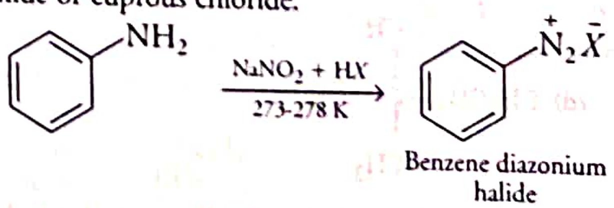


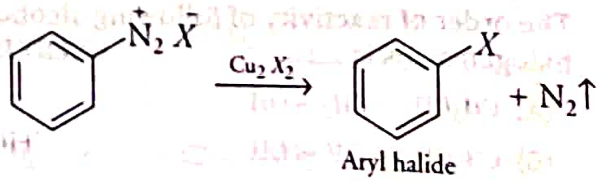


- o- and p-isomers can be easily separated due to large difference in their melting points.
- Reaction with iodine is reversible and require the presence of an oxidising agent (HNO_3, HIO_4) to oxidise the HI formed during iodination.
- The reaction with fluorine is violent and uncontrollable, hence fluoroarene cannot be prepared by direct fluorination of aromatic hydrocarbon.

From Diazonium Salts (Sandmeyer's Reaction)

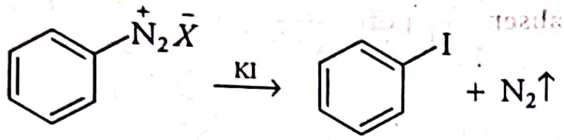
The diazonium salt is prepared by treating aniline dissolved in cold aqueous mineral acid with an aqueous solution of sodium nitrite at low temperature (0-5°C). Bromo and chloroarenes can be prepared by treating a freshly prepared diazonium salt solution with cuprous bromide or cuprous chloride.



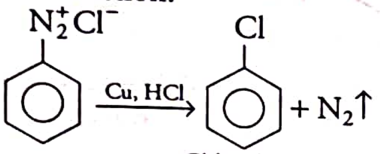


(X = Cl, Br)

Replacement of the diazonium group by iodine is done simply by shaking the diazonium salt with potassium iodide.

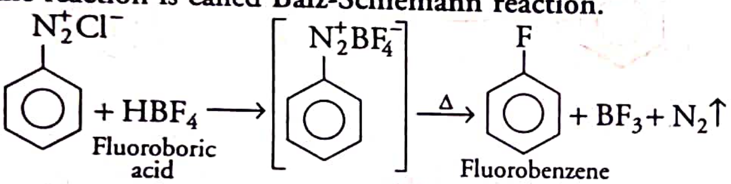


The Sandmeyer's reaction has been modified by using copper powder in place of cuprous halide. This reaction is called **Gattermann reaction.**



Chlorobenzene

If the diazonium group is replaced using fluoroboric acid, the reaction is called **Balz-Schiemann reaction.**



TOPIC PRACTICE 2

OBJECTIVE Type Questions

1. Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature? **NCERT Exemplar**

(a) $CH_3CH_2—CH_2—OH$

(b) $CH_3CH_2—\underset{\displaystyle CH_3}{\underset{|}{C}}H—OH$

(c) $CH_3CH_2—\underset{\displaystyle CH_3}{\underset{|}{C}}H—CH_2OH$

(d) $CH_3CH_2—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}—OH$

2. The order of reactivity of following alcohols with halogen acids is .... **NCERT Exemplar**

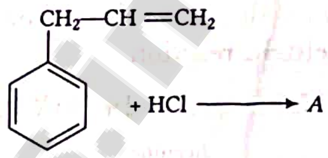
(A) $CH_3CH_2—CH_2—OH$

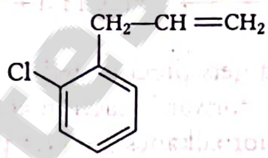
(B) $CH_3CH_2—\underset{\displaystyle CH_3}{\underset{|}{C}}H—OH$

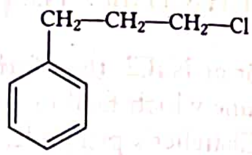
(C) $CH_3CH_2—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}—OH$

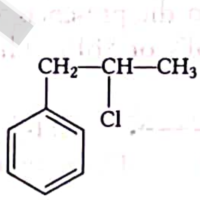
(a) (A) > (B) > (C) (b) (C) > (B) > (A)
(c) (B) > (A) > (C) (d) (A) > (C) > (B)

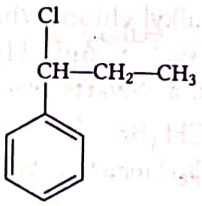
3. What is '*A*' in the following reaction? **NCERT Exemplar**



(a) 

(b) 

(c) 

(d) 

4. Alkyl halides are prepared from alcohols by treating with

(a) $HCl + ZnCl_2$ (b) Red P + Br_2
(c) $H_2SO_4 + KI$ (d) Both (a) and (b)

5. Select the by-product formed in the reaction,

$$ROH + PCl_5 \longrightarrow RCl + A$$

Here *A* is

(a) $POCl_3 + HCl$
(b) H_3PO_3 + No other by-product
(c) $H_3PO_3 + HCl$
(d) $POCl_3$ +No other by-product

6. Which reagent will you use for the following reaction? **NCERT Exemplar**

$$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

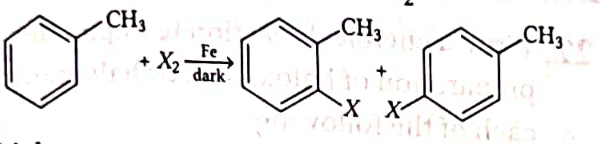
(a) Cl_2 / UV light (b) NaCl + H_2SO_4
(c) Cl_2 gas in dark
(d) Cl_2 gas in the presence of iron in dark

7. Which of the following is halogen exchange reaction? **NCERT Exemplar**

(a) $RX + NaI \rightarrow RI + NaX$

(b) $>C=C< + HX \longrightarrow >\underset{\displaystyle H}{\underset{|}{C}}—\underset{\displaystyle X}{\underset{|}{C}}<$

(c) $R—OH + HX \xrightarrow{ZnCl_2} R—X + H_2O$

(d) 

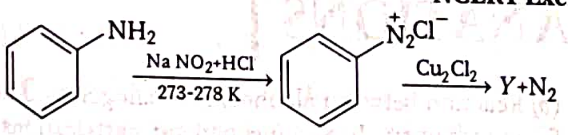
8. Which reagents are required for one step conversion of chlorobenzene to toluene? **CBSE SQP (Term I)**

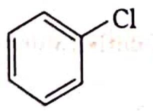
(a) $CH_3Cl / AlCl_3$
(b) CH_3Cl, Na, Dry ether
(c) CH_3Cl / Fe dark
(d) $NaNO_2/HCl/0\text{-}5°C$

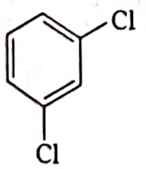
9. Toluene reacts with a halogen in the presence of iron (III) chloride giving *ortho* and *para* halo compounds. The reaction is **NCERT Exemplar**

(a) electrophilic elimination reaction
(b) electrophilic substitution reaction
(c) free radical addition reaction
(d) nucleophilic substitution reaction

10. Identify the compound *Y* in the following reaction. **NCERT Exemplar**



(a)  (b) 

(c)  (d) 

VERY SHORT ANSWER Type Questions

11. Identify the products *A* and *B* formed in the following reaction.

$$CH_3—CH_2—CH=CH—CH_3 + HCl \longrightarrow A + B$$

NCERT Exemplar

12. Write the structures and names of the compounds formed, when compound *A* with molecular formula C_7H_8, is treated with Cl_2 in the presence of $FeCl_3$. **NCERT Exemplar**

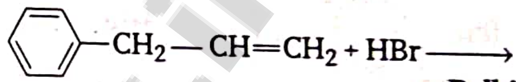
13. Name the alkene which will yield 1-chloro-1-methylcyclohexane by its reaction with HCl. Write the reactions involved.

14. Give one example of alkene where addition of HBr gives same product in the presence or absence of peroxide.

SHORT ANSWER Type I Questions

15. Draw the structures of major monohalo products in each of the following reactions.

(i) 

(ii) 

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16. How will you carry out the following conversions?

(i) 2-bromopropane to 1-bromopropane
(ii) Benzene to *p*-chloronitrobenzene

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17. Write the structure of the major organic products in each of the following reactions.

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow[Heat]{Acetone}$
(ii) $CH_3CH_2CH_2OH + SOCl_2 \xrightarrow{Pyridine}$
(iii) $CH_3CH_2CH=CH_2 + HBr \xrightarrow{Peroxide}$
(iv) $CH_3CH=C(CH_3)+HBr \longrightarrow$ (with CH_3 below the C) **NCERT**

18. Why aryl halides cannot be prepared by the reaction of phenol with HCl in the presence of $ZnCl_2$? **NCERT Exemplar**

19. A hydrocarbon, C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound, C_5H_9Cl in bright sunlight. Identify the hydrocarbon. **NCERT**

SHORT ANSWER Type II Questions

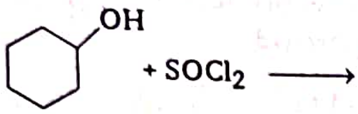
20. Among the following alcohols, which will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?

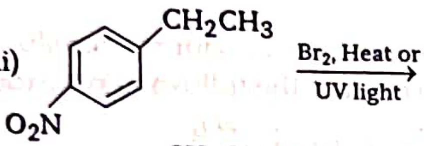
$CH_3—CH_2—CH(CH_3)—CH_2OH$,

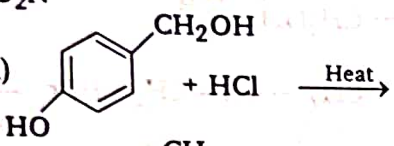
$CH_3CH_2—C(CH_3)_2—OH$,

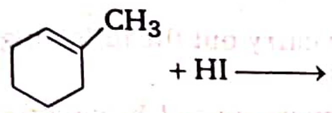
$CH_3—CH_2—CH_2—CH(CH_3)—OH$

21. Draw the structures of major monohalo products in each of the following reactions.

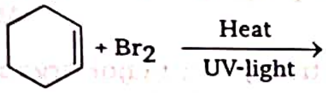
(i) 

(ii) 

(iii) 

(iv) 

(v) $CH_3CH_2Br + NaI \longrightarrow$

(vi) 

NCERT Intext

LONG ANSWER Type Questions

22. Write a chemical reaction to depict the preparation of haloalkane or haloarene from each of the following.

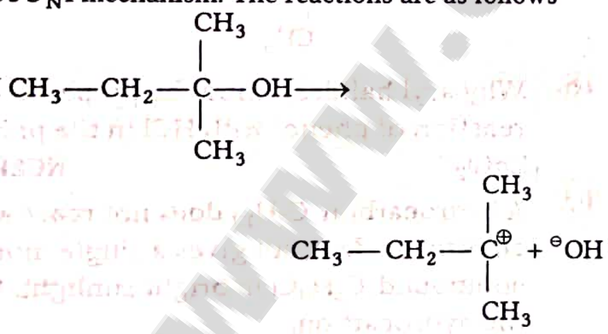
(i) Ethyl alcohol
(ii) Toluene
(iii) Aniline
(iv) Propene

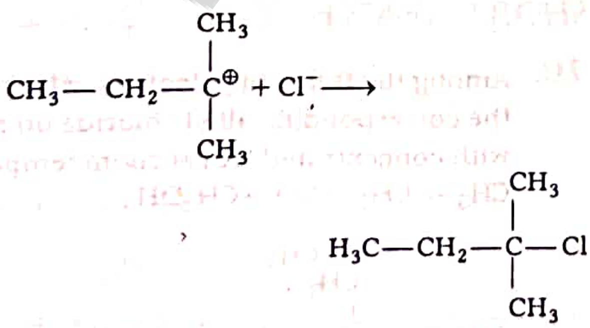
23. Among the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields

(i) a single monochloride.
(ii) three isomeric monochlorides.
(iii) four isomeric monochlorides. **NCERT Intext**

HINTS AND EXPLANATIONS

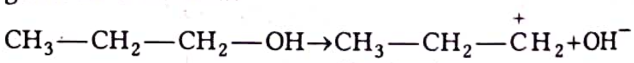
1. (*d*) When alcohols are treated with conc. HCl at room temperature then alkyl chloride is formed. This reaction follows S_N1 mechanism. The reactions are as follows

***Step* I** 

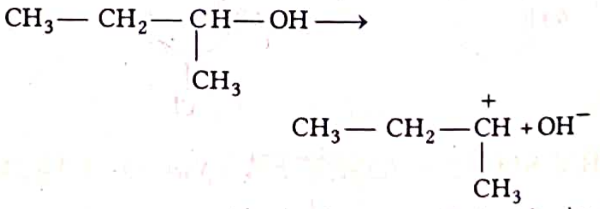
***Step* II** 

2. (*b*) Reaction between alcohols and halogen acid follows S_N1 mechanism. In S_N1 mechanism, carbocations are formed as intermediates.

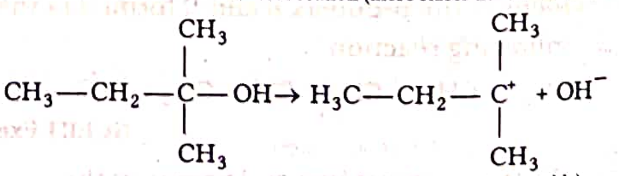
Let us consider the formation of carbocations with the given three alcohols.



1° carbocation (Least stable)



2° carbocation (more stable than 1° carbocation)



3° carbocation (most stable)

The tertiary carbocation is most stable so the possibilities of attack of X^- ion are more prominent in case of tertiary

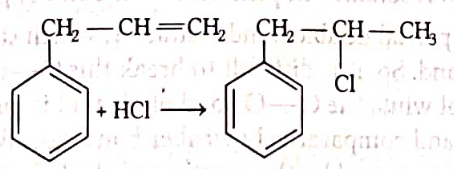
carbocations. Thus, attack of X^- ion to carbocation is proceeded with tertiary carbocation as follows

$$H_3C-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C^{\oplus}}}}} + X^- \longrightarrow H_3C-CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-X$$

3°carbocation

So, the correct option is (b).

3. (*c*)In this reaction, addition of HCl takes place on doubly bonded carbons in accordance with Markownikoff's rule *i.e.*, addition of negative addendum will take place on that carbon which has lesser number of hydrogen.
Thus,



Hence, option (c) is correct.

4. (*d*) $ROH + HCl \xrightarrow{ZnCl_2} RCl + H_2O$

$ROH + Br_2 \xrightarrow{\text{Red P}} R\text{—}Br$

5. (*a*) $ROH + PCl_5 \longrightarrow R\text{—}Cl + POCl_3 + HCl$

6. (*a*) The given reaction is a substitution reaction. It involves the replacement of 1° and 2° hydrogen of alkanes by chlorine. It occurs in presence of ultraviolet light or at high temperature. The chlorination does not occur at room temperature in absence of light. The reaction involved are as follows :

Step 1 $\quad Cl-Cl \xrightarrow[\text{light}]{UV} 2\dot{C}l$

$\dot{C}l + CH_3-CH_2-CH_2-CH_3 \longrightarrow CH_3CH_2CH_2-\dot{C}H_2 + HCl$

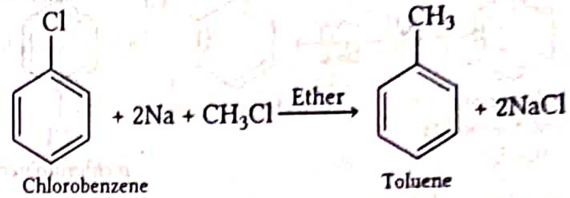
Step 2 $CH_3-CH_2-CH_2-\dot{C}H_2 + Cl_2 \longrightarrow CH_3-CH_2-CH_2-CH_2Cl + \dot{C}l$

Step 3 $CH_3-CH_2-CH_2-\dot{C}H_2 + \dot{C}l \longrightarrow CH_3CH_2CH_2CH_2Cl$

So, option (a) is the correct.

7. (*a*) Halogen exchange reactions are those reactions in which one halide replaces another. In option (a) halogen $(-X)$ is replaced by iodine. This reaction is named as Finkelstein reaction.
In option (b), there is the addition of hydrogen halide on alkene. In option (c), halogen replaces alcoholic group. While in option (d) halogen replaces the hydrogen of benzene ring.

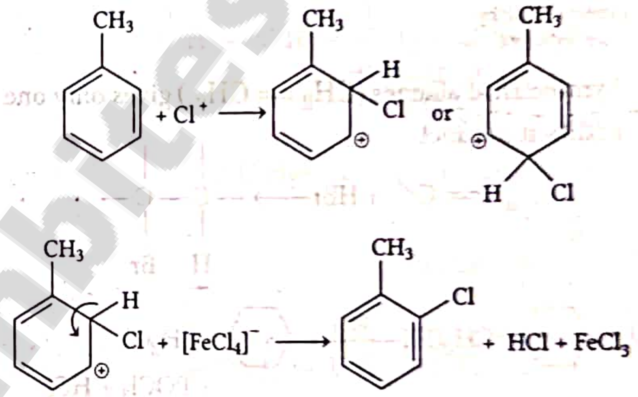
8. (*b*) CH_3Cl, Na, Dry ether



The above reaction is known as Wurtz fittig reaction.

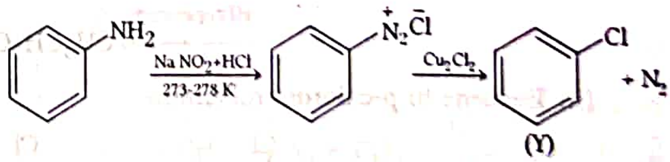
9. (*b*) Toluene reacts with a halogen in the presence of iron (III) chloride giving *ortho* and *para* halo compounds.The reaction is electrophilic substitution reaction.
It has the following mechanism

$$Cl-Cl \xrightarrow{FeCl_3} FeCl_4^- + Cl^+$$



In this mechanism, electrophile Cl^+ attacks to electron rich benzene ring and replaces hydrogen. So, the reaction is electrophilic substitution reaction.

10. (*a*) When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid and treated with sodium nitrite, a diazonium salt is formed. When this freshly prepared diazonium salt is mixed with cuprous chloride, then diazonium group is replaced by — Cl. Then chlorobenzene is formed which is *Y* in this reaction.



Hence, option (a) is correct.

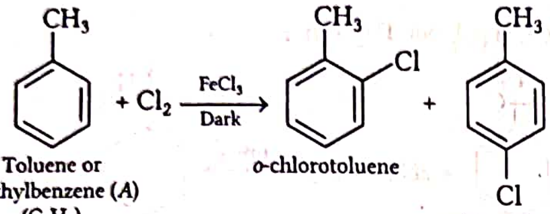
11. In the given reaction, addition occurs and following two products (*A* and *B*) are possible.

$$H_3C-CH_2-CH=CH-CH_3 + HCl \longrightarrow CH_3-CH_2-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$$

2-chloropentane (*A*)

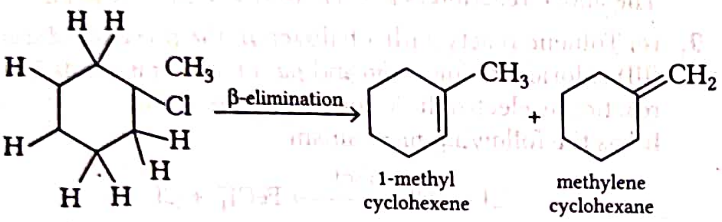
$$+\ CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-CH_3$$

3-chloropentane (*B*)

12. 

Toluene or Methylbenzene (A) (C_7H_8) $\xrightarrow[\text{Dark}]{FeCl_3}$ o-chlorotoluene + p-chlorotoluene

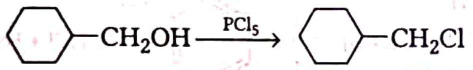
13. 1-methylcyclohexene.



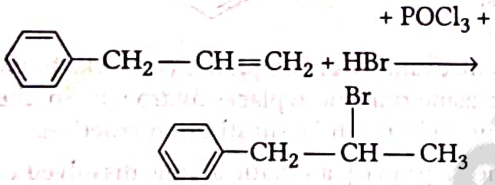
1-chloro-1-methyl cyclohexane $\xrightarrow{\beta\text{-elimination}}$ 1-methyl cyclohexene + methylene cyclohexane

14. Symmetrical alkenes ($CH_2 = CH_2$) gives only one addition product,

$$>C=C< + HBr \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{Br}{\overset{|}{\underset{|}{C}}}-$$

15. (i) 

$$\text{C}_6\text{H}_{11}-CH_2OH \xrightarrow{PCl_5} \text{C}_6\text{H}_{11}-CH_2Cl + POCl_3 + HCl$$

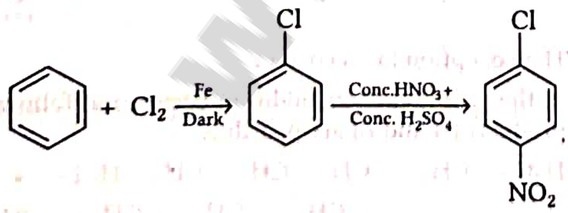
(ii) 

$$C_6H_5-CH_2-CH=CH_2 + HBr \longrightarrow C_6H_5-CH_2-\underset{}{\overset{Br}{\overset{|}{CH}}}-CH_3$$

16. (i) 2-bromopropane to 1-bromopropane

$$CH_3-\underset{Br}{\underset{|}{CH}}-CH_3 \xrightarrow{Alc.KOH} CH_3-CH=CH_2 \xrightarrow{HBr,\ peroxide} CH_3CH_2CH_2Br$$

(ii) Benzene to p-chloronitrobenzene



17. (i) $CH_3CH_2-CH_2-Cl + NaI \xrightarrow[\text{Heat}]{\text{Acetone}} CH_3CH_2CH_2I + NaCl$

1-chloropropane

(ii) $CH_3CH_2CH_2OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3CH_2CH_2Cl + SO_2\uparrow + HCl\uparrow$

Propan-1-ol → 1-chloropropane

(iii) $CH_3CH_2-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2CH_2Br$

But-1-ene → 1-bromobutane

(iv) $CH_3CH=\overset{CH_3}{\overset{|}{C}}-CH_3 + HBr \xrightarrow[\text{rule}]{\text{Markovnikov's}} CH_3-CH_2-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

2-bromo -2-methyl butane

18. Due to resonance in phenol, C—O bond of phenol has some partial double bond character, which strengthens the bond. So, it is difficult to break this C—O bond of phenol while the C—O bond of alcohol is purely single bond and comparatively weaker bond. So, alkyl halides can be prepared by the reaction of alcohols with HCl in the presence of $ZnCl_2$ while aryl halides cannot be prepared by the reaction of phenol with HCl in the presence of $ZnCl_2$.

$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow[ZnCl_2]{HCl} \text{No reaction}$$

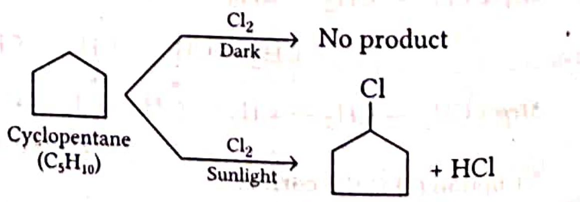
$$\underset{\text{Alcohol}}{RCH_2OH} \xrightarrow[ZnCl_2]{HCl} \underset{\text{Alkyl chloride}}{RCH_2Cl} + H_2O$$

19. Enlist the possibilities of structures for molecular formula, C_5H_{10} which react in dark and in sunlight. In the given reaction,

(i) Molecular formula C_5H_{10} can be either alkene or cycloalkane.

(ii) Since, the hydrocarbon does not react with chlorine in dark, hence, it is not an alkene but is a cycloalkane.

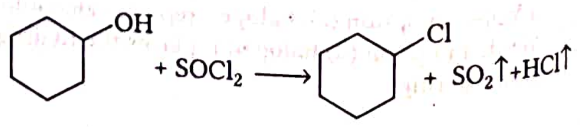
(iii) Since, it forms only single monochloro derivative in bright sunlight, all the H-atoms should be identical. So, it is cyclopentane.



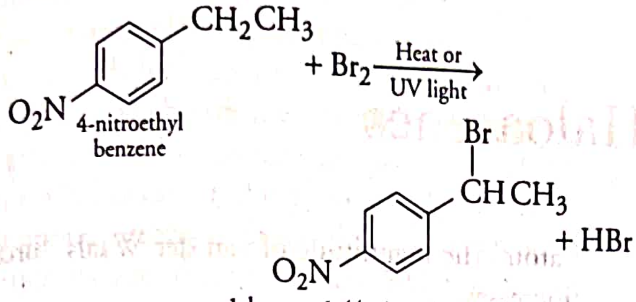
Cyclopentane (C_5H_{10}) $\xrightarrow[\text{Dark}]{Cl_2}$ No product

Cyclopentane (C_5H_{10}) $\xrightarrow[\text{Sunlight}]{Cl_2}$ Chlorocyclopentane (C_5H_9Cl) + HCl

20. 3° alcohols are very reactive and hence, their reactions with conc. HCl takes place even at room temperature.

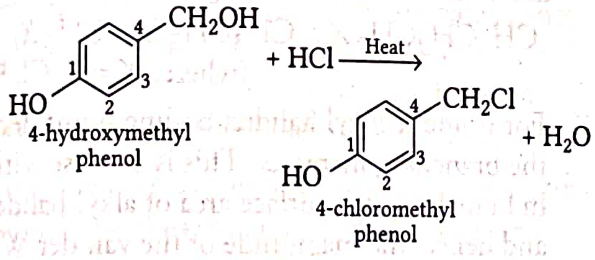
21. (i) 

Cyclohexanol + $SOCl_2$ ⟶ Chlorocyclohexane + $SO_2\uparrow + HCl\uparrow$

(ii) 

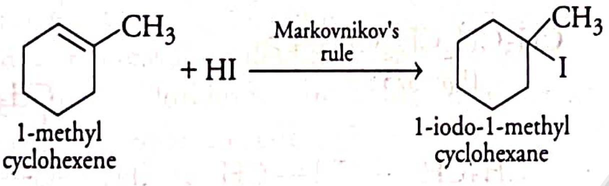
4-nitroethyl benzene; 1-bromo-1-(4-nitrophenyl) ethane

Bromination does not take place on benzene ring.

(iii) 

4-hydroxymethyl phenol; 4-chloromethyl phenol

Note Phenolic —OH group is not replaced by —Cl group.

(iv) 

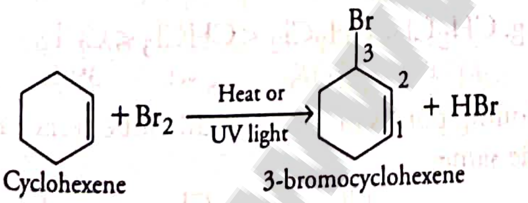
1-methyl cyclohexene; 1-iodo-1-methyl cyclohexane

According to Markovnikov's rule, iodine will add to the carbon atom having less number of hydrogen atoms.

(v) $CH_3CH_2Br + NaI \longrightarrow CH_3CH_2I + NaBr$

Bromoethane → Iodoethane

Iodide ion is a strong nucleophile, so it displaces bromide ion.

(vi) 

Cyclohexene; 3-bromocyclohexene

Under the conditions specified above, allylic halogenation takes place. Addition reaction can take place only at room temperature.

22. (i) Refer to text on page 216

(ii) Refer to text on page 217.

(iii) Refer to text on page 217 and 218

(iv) Refer to text on page 216

23. (i) A single monochloride (IV) can be produced only when all the hydrogen atoms are equivalent. This isomer must be symmetrical. Its structure is given by (I).

$$H_3C-C(CH_3)_2-CH_3 + Cl_2 \xrightarrow{h\nu} H_3C-C(CH_3)_2-CH_2Cl + HCl$$

(I) → (IV) 1-chloro-2, 2-dimethylpropane

(ii) Isomer (II) has three groups of equivalent hydrogen atoms. Therefore, three isomeric monochlorides (V, VI and VII) are produced.

$$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_3 + Cl_2 \xrightarrow{h\nu}$$

Pentane (II)

$$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-Cl$$

1-chloropentane (V)

$$+\ \overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H(Cl)-\overset{1}{C}H_3$$

2-chloropentane (VI)

$$+\ \overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H(Cl)-\overset{2}{C}H_2-\overset{1}{C}H_3$$

3-chloropentane (VII)

(iii) Isomer (III) has four groups of equivalent hydrogen atoms. Therefore, it can produce four isomeric monochlorides (VIII, IX, X and XI).

$$\overset{1}{C}H_3-\overset{2}{C}H(CH_3)-\overset{3}{C}H_2-\overset{4}{C}H_3 + Cl_2 \xrightarrow{h\nu}$$

2-methylbutane (III)

$$Cl-H_2\overset{1}{C}-\overset{2}{C}H(CH_3)-\overset{3}{C}H_2-\overset{4}{C}H_3 + \overset{1}{C}H_3-\overset{2}{C}(Cl)(CH_3)-\overset{3}{C}H_2-\overset{4}{C}H_3$$

1-chloro-2-methylbutane (VIII); 2-chloro -2-methyl butane (IX)

$$+\ \overset{4}{C}H_3-\overset{3}{C}H(CH_3)-\overset{2}{C}H(Cl)-\overset{1}{C}H_3 + \overset{4}{C}H_3-\overset{3}{C}H(CH_3)-\overset{2}{C}H_2-\overset{1}{C}H_2-Cl$$

2-chloro -3-methylbutane (X); 1-chloro -3-methylbutane (XI)

|TOPIC 3|
Properties of Haloalkanes and Haloarenes

PHYSICAL PROPERTIES OF HALOALKANES AND HALOARENES

Some of the important physical properties of haloalkanes and haloarenes are as follows:

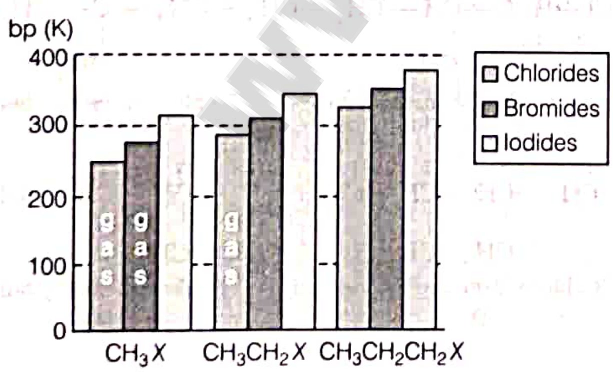
(i) **Physical state** Alkyl halides are colourless when they are pure. However, bromides and iodides develop colour when exposed to light. Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are gases at room temperature. Higher members are liquids or solids. Many volatile halogen compounds have sweet smell.

(ii) **Melting and boiling points** Molecules of organic halogen compounds are generally polar. Due to greater polarity and higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals') between molecules are stronger in the halogen derivatives.

That's why, the boiling points of chlorides, bromides and iodides are higher than those of the hydrocarbons of comparable molecular mass.

As the molecular mass increases, the melting and boiling points increases. The attractions get stronger as the molecules get bigger in size and have more electrons.

The pattern of variation of boiling points of different halides is depicted in table given below:



Comparison of boiling points of some alkyl halides

- For the same alkyl group, the boiling point of alkyl halides decreases in the order $RI > RBr > RCl > RF$, because with increase in size and mass of halogen atom, the magnitude of van der Waals' forces increases.
- As the size of alkyl group decreases, boiling points decrease for the same halogen atom.

$$CH_3CH_2CH_2X > CH_3CH_2X > CH_3X$$
(where, X = F, Cl, Br and I)

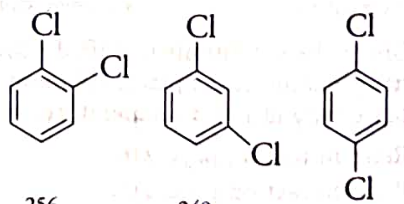
For isomeric alkyl halides, boiling point decreases as the branching increases. This is because with increase in branching, the surface area of alkyl halide decreases and hence, the magnitude of the van der Waals' forces of attraction decreases.

$$\underset{(bp=375\,K)}{CH_3CH_2CH_2CH_2Br} > \underset{(bp=364\,K)}{CH_3CH_2-\underset{\underset{Br}{|}}{CH}-CH_3} > \underset{(bp=346\,K)}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3}$$

- Generally, the boiling points of chloro, bromo and iodo compounds increases as the number of halogen atom increases.

e.g. $\underset{249\,K}{CH_3Cl} < \underset{313\,K}{CH_2Cl_2} < \underset{334\,K}{CHCl_3} < \underset{350\,K}{CCl_4}$

Boiling points of isomeric dihalobenzenes are nearly the same.



mp/K	256	249	323
bp/K	453	446	448

However, the *p*-isomers have high melting point as compared to their *o*-and *m*-isomers. This is due to the symmetry of *p*-isomers that fits in the crystal lattice better as compared to *o*- and *m*-isomers.

(iii) **Density** Fluoro and chloroalkanes are lighter than water while bromo, iodo and polychloro derivatives are heavier than water. With the increase in the number of C-atoms, halogen atoms and atomic mass of halogen atom, density increases.

(iv) **Solubility** For haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is released when new attractions are set up between haloalkane and the water molecules as these are not strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low.

They are soluble in organic solvents because the new intermolecular attractions between haloalkanes and solvent molecules are of same strength as the ones being broken that exists separately between the alkyl halide molecules and solvent molecules.

(v) **Stability** The stability also decreases as the strength of C—X bond decreases (RF > RBr > RCl > RI).

(vi) **Dipole moment** As the electronegativity of the halogen decreases from Cl to I, dipole moment also decreases whereas fluorides have lower dipole moment than chlorides because of very small size of F which outweighs the effect of greater electronegativity.

$$CH_3Cl > CH_3F > CH_3Br > CH_3I$$

CHEMICAL REACTIONS OF HALOALKANES

Due to the presence of a polar C—X bond, haloalkanes are highly reactive compounds. The reactions may be divided into following categories:

Nucleophilic Substitution Reactions

When a nucleophile (i.e. electron rich species) stronger than the halide ion, reacts with haloalkane having a partial positive charge on the carbon atom bonded to halogen, a substitution reaction takes place and the halogen atom called leaving group departs as halide ion. Since, the substitution reaction is initiated by a nucleophile, hence it is called nucleophilic substitution reaction.

$$\ddot{Nu}^- + \;>\overset{\delta+}{C}-\overset{\delta-}{X} \longrightarrow \;>C-Nu + X^-$$

Nucleophilic substitution of alkyl halides (R—X)

$$R-X + Nu^- \longrightarrow R-Nu + X^-$$

Reagent	Nucleophile (Nu^-)	Substitution product (R—Nu)	Class of main product
NaOH(KOH)	HO^-	ROH	Alcohol
H_2O	H_2O	ROH	Alcohol
NaOR'	$R'O^-$	ROR'	Ether
NaI	I^-	R—I	Alkyl iodide
NH_3	NH_3	$R\,NH_2$	Primary amine
$R'NH_2$	$R'NH_2$	$RNHR'$	sec-amine
$R'R''NH$	$R'R''NH$	$RNR'R''$	*tert*-amine
KCN	$\bar{C}\equiv N:$	RCN	Nitrile (cyanide)
AgCN	Ag—CN:	RNC (isocyanide)	Isonitrile
KNO_2	$O=N-O^-$	$R-O-N=O$	Alkyl nitrite
$AgNO_2$	$Ag-O-\ddot{N}=O$	$R-NO_2$	Nitroalkane
R'COOAg	$R'COO^-$	R'COOR	Ester
$LiAlH_4$	H^-	RH	Hydrocarbon
R^-M^+	R^-	RR'	Alkane

Groups like cyanides and nitrites possess two nucleophilic centres and are called **ambident nucleophiles.** Cyanide group is a hybrid of two contributing structures and therefore, can act as nucleophile in two different ways

$$[\,^-:C\equiv N: \leftrightarrow :C=\ddot{N}\,].$$

When it links through carbon atom, it results in formation of **alkyl cyanides**, while that through nitrogen atom, it results in formation of **isocyanides.**

Similarly, in nitrite ion. There are two different points of linkage ($^-O-\ddot{N}=O$). The linkage through oxygen results in **alkyl nitrites** while that through nitrogen atom, results in **nitroalkanes.**

Note Among alkyl halides, iodide ion is the best leaving group and hence, iodoalkanes undergo nucleophilic substitution reactions at the fastest rate in comparison to fluoroalkane, as fluoride ion is the poorest leaving group. Better the leaving group, more facile is the nucleophilic substitution reaction.

Nucleophilic substitution reactions of alkyl halides ($R—X$) are as follow:

Reactions	Nucleophiles
$R—X \xrightarrow{+aq.\ KOH} ROH + KX$; Alcohol	$(H\bar{O})$
$R—X \xrightarrow{+Na^+\bar{O}R'} ROR' + NaX$; Ether	$(R'\bar{O})$
$R—X \xrightarrow{+H_2O} ROH$; Alcohol	(H_2O)
$R—X \xrightarrow{+KCN} R—CN + KX$; Alkyl cyanide	$(—C{\equiv}N)$
$R—X \xrightarrow{+AgCN} R—NC + AgX$; Alkyl isocyanide	$(Ag—C{\equiv}N:)$
$R—X \xrightarrow{+KNO_2} R—O—N{=}O + KX$; Alkyl nitrite	$(O{=}N—\bar{O})$
$R—X \xrightarrow{+AgNO_2} R—NO_2 + AgX$; Nitroalkane	$(Ag—O—\ddot{N}{=}O)$
$R—X \xrightarrow{+R'—C(=O)—O—Ag} R'—C(=O)—O—R + AgX$; Ester	$(R'COO^-)$
$R—X \xrightarrow{+LiAlH_4} R—H$; Alkane	$(\bar{H})$
$R—X \xrightarrow{+NH_3} R—NH_2$; 1° amine	(NH_3)
$R—X \xrightarrow{+\overset{+}{Na}\bar{C}{\equiv}CH} R—C{\equiv}CH + NaX$; Higher alkyne	$(\bar{C}{\equiv}CH)$
$R—X \xrightarrow{R^-M^+} R—R' + MX$; Alkane	$(\bar{R'})$

($R—X$: Alkyl halides)

EXAMPLE |1| Haloalkanes react with KCN to form alkyl cyanides while AgCN forms isocyanides as the chief product. Why?

Sol. K^+CN^- is predominantly ionic and provides cyanide ions in solution. Although, both carbon and nitrogen atoms are in position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since, C— C bond is more stable than C— N bond. However, Ag— CN is mainly covalent in nature and only electron pair of nitrogen is available for bond formation . As a result, alkyl isocyanides are the chief products.

EXAMPLE |2| Haloalkanes react with KNO_2 to form alkyl nitrites while $AgNO_2$ forms nitroalkanes as the chief product. why?

Sol. KNO_2 (or $O{=}N—O^-K^+$) is predominantly ionic and one of the oxygen atom have a negative charge. Nucleophilic attack through this negatively charged oxygen atom on the alkyl halides mainly gives alkyl nitrites. In contrast, $AgNO_2$ is a covalent compound and both oxygen and nitrogen atoms carry lone pair of electrons. Since, nitrogen is less electronegative than oxygen, therefore, lone pair of electrons of nitrogen is more easily available for bond formation. As a result, nitroalkanes are the chief products.

Mechanism

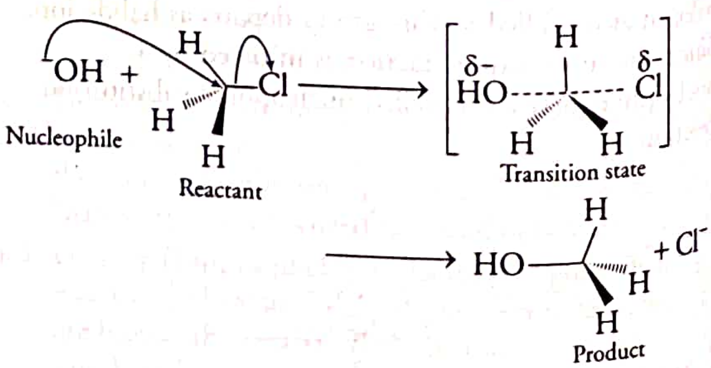
The nucleophilic substitution reactions proceed by the following two different mechanisms:

I. Bimolecular Nucleophilic Substitution (S_N2)

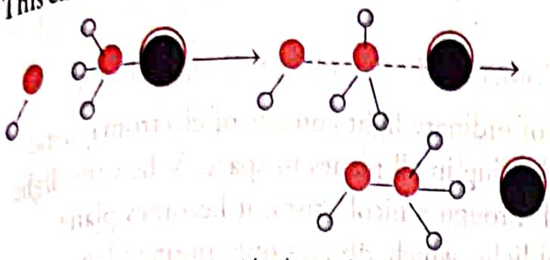
When two molecules take part in determining the rate of the reaction, it is called bimolecular nucleophilic substitution (S_N2).

Here, the rate depends upon the concentration of both the reactants.

e.g. The reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion follow a second order kinetics.



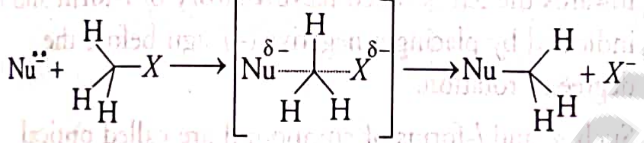
This can be represented diagrammatically as shown below:



Grey dot represents the incoming hydroxide ion and black dot represents the outgoing halide ion

In S_N2 mechanism, the incoming nucleophile approaches the alkyl halide (CH_3X) molecule and starts interacting with it due to which the carbon-halide ($C—X$) bond starts breaking and a new carbon-nucleophile (C—OH) bond starts forming. These two processes take place simultaneously in a single step and no intermediate is formed.

Such reaction occurs through the formation of a transition state. In transition state, the C-atom is simultaneously bonded to incoming nucleophile and also to the outgoing leaving group, i.e. carbon is bonded to five atoms. Thus, this state is unstable and results in the formation of the product.



Transition state

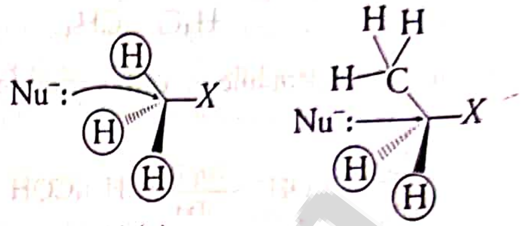
In S_N2 reactions, the attack of nucleophile (i.e. Nu^-) occurs from the backside and the leaving group leaves from the front side. As this happens, the configuration of C-atom under attack invert in the same way as an umbrella is turned inside out when caught in a strong wind, while the leaving group is pushed away, this process is called **inversion of configuration** or **Walden inversion** and is a characteristic feature of S_N2 reaction.

Since, S_N2 requires the backside approach of nucleophile to the carbon bearing the leaving group, i.e. X-atom, the presence of bulky alkyl groups blocks the approach of the nucleophile to carbon due to steric hindrance. That's why the simple alkyl halides, methyl halides and primary alkyl halides always react predominantly by S_N2 mechanism.

Tertiary halides are least reactive because of the presence of bulky groups which hinders the approaching nucleophiles. Non-polar solvents favour S_N2 mechanism.

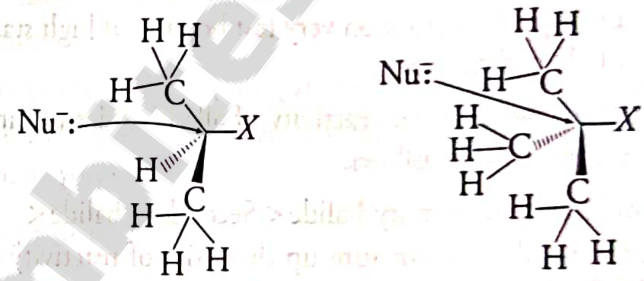
Thus, the order of reactivity of alkyl halides towards S_N2 reactions is as follows:

Methyl halide > Primary halide (1°)



Methyl   Ethyl, 1°

Secondary halide (2°) > Tertiary halide (3°)



iso-propyl, 2°   *tert*-butyl, 3°

Steric effects in S_N2 reaction

II. Unimolecular Nucleophilic Substitution (S_N1)

When only one molecule is involved in determining the rate of the reaction, it is called unimolecular nucleophilic substitution. Such type of reactions are generally carried out in polar protic solvents such as water, alcohol, acetic acid, etc., because they stabilise the carbocation by solvation.

Mechanism

S_N1 reaction occurs via two steps:

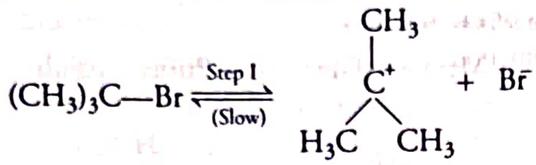
In *step* I, formation of carbocation takes place due to the heterolytic cleavage of $\geqslant C—X$ bond. This step is slow and reversible (rate determining step). This step involves only one reactant, i.e. alkyl halide, therefore, rate of reaction depends only on the concentration of alkyl halide and not on the concentration of nucleophile.

In *step* II, nucleophile attack the carbocation formed in step I and the substitution reaction completes.

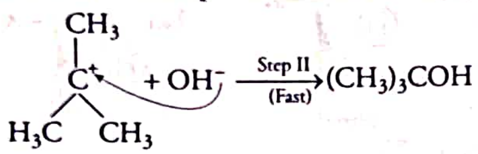
e.g. The reaction between *tert*-butyl bromide and hydroxide ion yield *tert*-butyl alcohol.

$$(CH_3)_3C—Br + OH^- \longrightarrow (CH_3)_3COH + Br^-$$

Step I Formation of carbocation intermediate



Step II Attack of nucleophile on carbocation formed



- Greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. That's why, 3° alkyl halides undergo S_N1 reaction very fast because of high stability of 3° carbocations.

Therefore, the order of reactivity of alkyl halides toward S_N1 reactions is as follows:

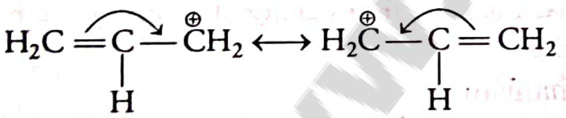
Methyl halide < Primary halide < Secondary halide < Tertiary halide We can sum up the order of reactivity of alkyl halide towards S_N1 and S_N2 reactions as follows:

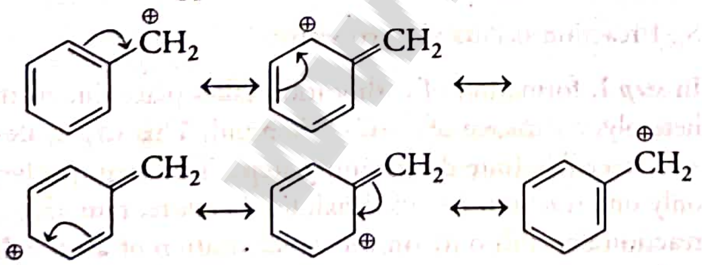
S_N1 reactivity increases ←

Tertiary halide, Secondary halide, Primary halide, CH_3X

→ S_N2 reactivity increases

Allylic and benzylic halides show high reactivity towards the S_N1 reaction because carbocation thus formed gets stabilised through resonance.





- For a given alkyl group, the reactivity of the halide, $R—X$ follows the same order in both the mechanisms, S_N1 and S_N2.

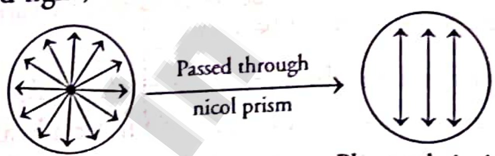
$$R—I > R—Br > R—Cl > R—F$$

Stereochemical Aspects of Nucleophilic Substitution Reactions

S_N2 reaction proceeds with the complete stereochemical inversion while S_N1 reaction proceeds with racemisation. To understand this concept, some basic stereochemical principles and notations are need to be learnt, which are given as follows:

Plane Polarised Light and Optical Activity

A beam of ordinary light consists of electromagnetic waves vibrating in all planes in space. When this light is passed through a nicol prism, it becomes plane polarised light, which vibrates only in one plane.



Polarisation of ordinary light

When the solutions of certain organic compounds are placed in the path of plane polarised light, they rotate the path of the light either to left or right, such substances are called **optically active substances.**

A substance which rotates the plane polarised light to the right is called **dextrorotatory** or ***d*-form** and is indicated by placing a positive (+) sign before the degree of rotation.

The substance which rotates the plane polarised light towards the left is called **laevorotatory** or ***l*-form** and is indicated by placing a negative (–) sign before the degree of rotation.

Such *d*-and *l*-forms of compound are called **optical isomers** and the phenomenon is called **optical isomerism.** The angle through which the plane polarised light is rotated can be measured by an instrument called **polarimeter.**

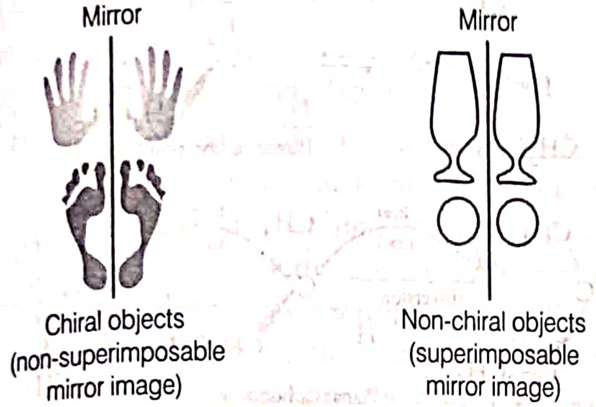
Molecular Asymmetry, Chirality and Enantiomers

The four valencies of carbon atom are directed towards the corners of regular tetrahedron and if all the atoms or groups attached to a carbon atom are different, such carbon atom is called **asymmetric carbon atom** or **stereocentre.** The resulting molecule would lack symmetry and the molecule is called **asymmetric molecule.** The asymmetry of the molecule is responsible for the optical activity in such organic compounds.

All molecules or objects have mirror images. An object or molecule which is not superimposable on its mirror image is called **chiral** and this property is called **chirality,** e.g. human hand.

If we hold our left hand in front of a mirror, the image looks like the right hand. If we try to superimpose left and right hands, by putting the one on the other one,

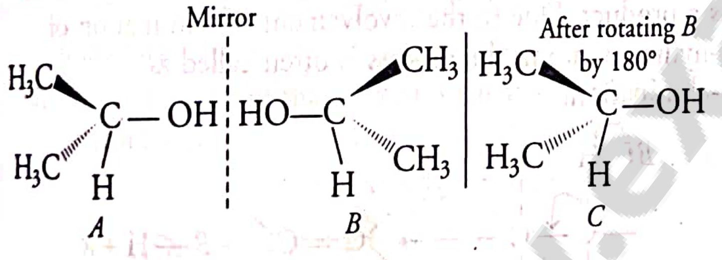
we observe that the hands cannot be superimposed, hence the hands are chiral.



Some common examples of chiral and achiral objects

The objects which are superimposable on their mirror images are called **achiral** as the glass and the sphere in the above figure.

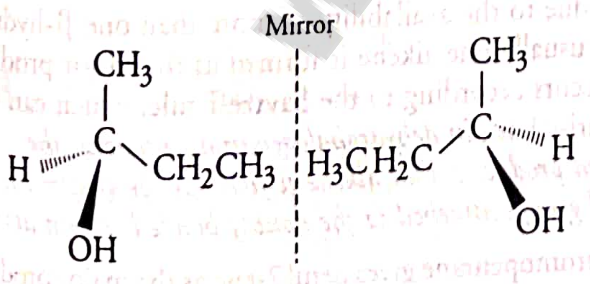
Let us take two simple molecules, propan-2-ol and butan-2-ol and their mirror images. Propan-2-ol does not contain asymmetric carbon atom. Therefore, it is achiral.



The structure *C* is superimposable on *A*.

Butan-2-ol molecule contains asymmetric carbon atom and as expected is chiral.

It has non-superimposable mirror images as shown in the figure:



Some common examples of chiral molecules are

2-chlorobutane, ($CH_3CH(Cl)CH_2CH_3$),
2,3-dihydroxy-propanal (OHC—CHOH—CH_2OH),
bromochloroiodomethane (BrClCHI),
2-bromopropanoic acid (H_3C—CHBr—COOH).

The optical isomers which are non-superimposable mirror images of each other are called **enantiomers** and the phenomenon is called **enantiomerism.**

The enantiomers have identical physical and chemical properties but differs with respect to the rotation of plane polarised light. If one of the enantiomer is dextrorotatory then other will be laevorotatory.

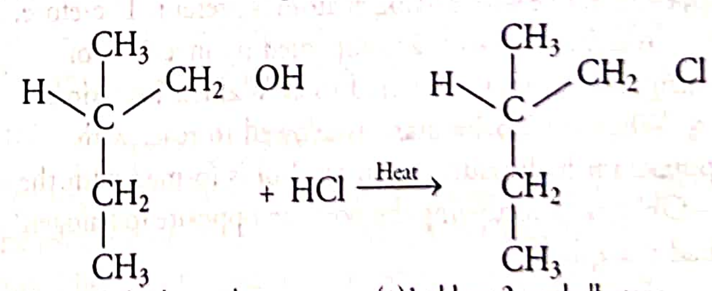
Racemic Mixtures and Racemisation

A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is called **racemic mixture.** It is represented as *dl* or ± forms and will be optically inactive.

The process of converting *d*- or *l*-form of an optically active compound into racemic form (*dl*) is called racemisation.

Retention

When the relative spatial arrangement of bonds to an asymmetric centre in a chiral molecule remains the same before and after the reaction, the reaction is said to occur with **retention of configuration**, e.g.



(–) 2-methyl-1-butanol (+)1-chloro-2-methylbutane

In the above example, no bond at the asymmetric carbon is broken, and the product will have the same general configuration of groups around the stereocentre as that of reactants.

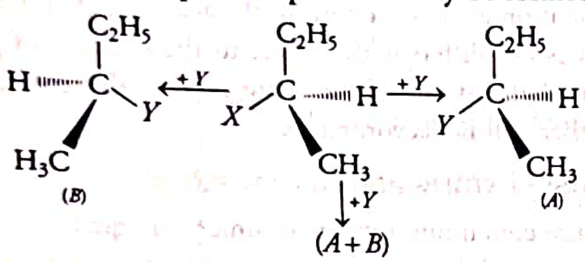
Therefore, the reaction proceeds with retention of configuration inspite of change of optical rotation from (–) to (+).

Inversion

If the relative spatial arrangement of bonds at an asymmetric carbon atom becomes opposite as compared to reactant after the reaction, then the reaction is called **inversion.**

Examples of Inversion, Retention and Racemisation

During the substitution of a group X by Y in the reactions given below, three possible products may be formed.

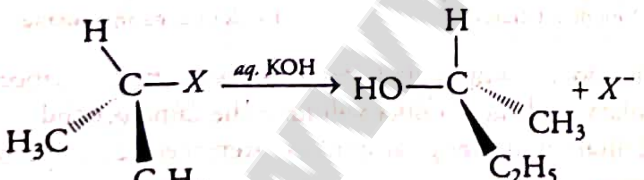


If A is the only product, the process is called **retention of configuration** because A has same configuration as that of reactant. If B is the only product, the process is called **inversion of configuration** because B has the configuration opposite to that of reactant. If an equimolar mixture i.e. 50 : 50 mixture of A and B is formed, the process is called **racemisation** and the product is optically inactive.

Now, stereochemical aspects of nucleophilic substitution reactions can easily be understood.

Stereochemical Aspects of S_N2 Reaction

In S_N2 mechanism, the nucleophile attacks on the side opposite to one where halogen atom is present. Therefore, S_N2 reaction is always accompanied by inversion of configuration, that is referred to as **Walden inversion**. e.g. When (–) 2-halobutane is allowed to react with potassium hydroxide, (+) butan-2-ol is formed with the —OH group occupying the position opposite to halogen had occupied.



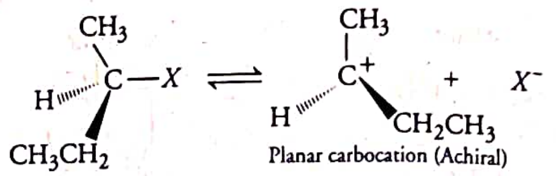
(–)2-halobutane (+) Butan-2-ol

Thus, S_N2 reaction of optically active alkyl halides is always accompanied by the inversion of configuration.

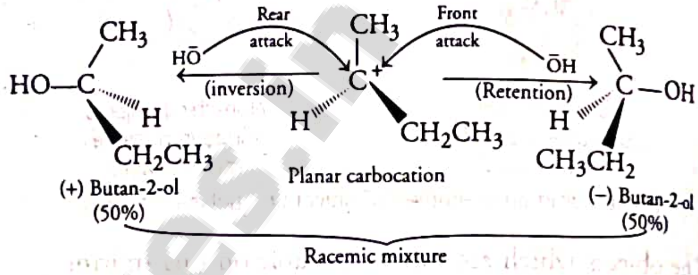
Stereochemical Aspects of S_N1 Reaction

In S_N1 reactions, if the alkyl halide is optically active, the product obtained is a racemic mixture. The intermediate carbocation formed in slowest step being sp^2 hybridised is planar (achiral) species.

Therefore, the attack of the nucleophile OH^- can occur from both the faces with equal ease of forming a mixture of two enantiomers. Thus, S_N1 reaction of optically active alkyl halides are accompanied by racemisation.

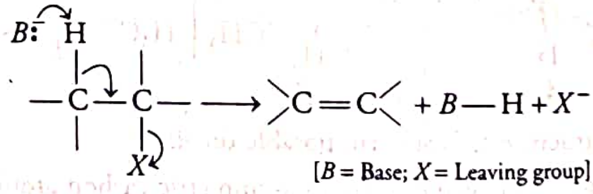


Planar carbocation (Achiral)



Elimination Reactions : Dehydrohalogenation (Formation of Alkenes)

When a haloalkane with β-hydrogen atom is heated with alc. KOH solution, then alkene is formed. In this reaction, hydrogen is eliminated from β-carbon and the halogen is lost from α-carbon atom. As a result, an alkene is formed as a product. Due to the involvement of elimination of β-hydrogen atom, the process is often called as β-elimination.

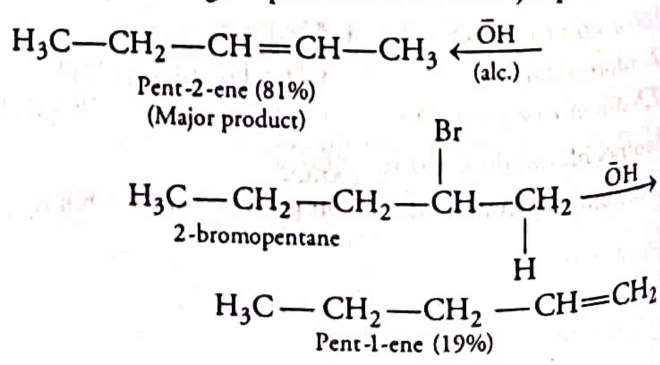


[B = Base; X = Leaving group]

e.g. $H—CH_2—CH_2Br + KOH\text{ (alc.)} \xrightarrow{\text{Heat}} CH_2 = CH_2 + KBr + H_2O$

If there is possibility for the formation of more than one alkene due to the availability of more than one β-hydrogen atoms, usually one alkene is formed as the major product. This occurs according to the **Saytzeff rule**, which can be summarised as *"in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms"*.

e.g. 2-bromopentane gives pent-2-ene as the major product.



Elimination *versus* Substitution

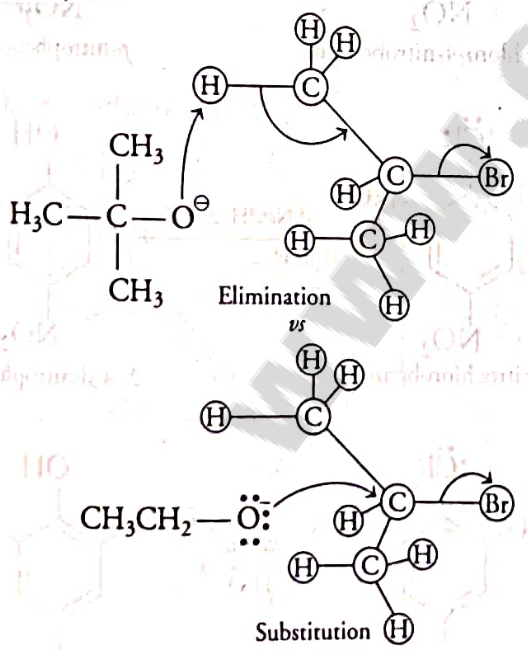
When alkyl halide reacts with nucleophile, it may undergo either substitution *via* S_N1 and S_N2 or elimination reaction.

It depends upon the following factors :

(i) **The nature of alkyl halide** Primary alkyl halide will prefer S_N2 reaction, i.e. nucleophilic substitution reaction *via* S_N2 mechanism. Secondary alkyl halide can undergo substitution or elimination depending upon the strength of the nucleophile.
Tertiary alkyl halide will undergo substitution or elimination depending upon the stability of carbocation or the more substituted alkene.

(ii) **The strength and size of the nucleophile or base** A bulkier nucleophile will carry out the elimination more easily than substitution as it prefers to act as a base and abstracts a proton rather than approaching a tetravalent carbon atom (due to steric reasons) and *vice-versa*. Stronger nucleophiles like $C_2H_5O^-$ will bring out the elimination whereas, nucleophiles like OH^- will bring out the substitution.

(iii) The conditions of the reaction such as temperature, pressure, etc.



Reaction with Metals

Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as **organometallic compounds.**

(i) Action with Magnesium (Formation of Grignard Reagents)

Victor Grignard in 1900 discovered an important class of organometallic compounds, i.e. alkyl magnesium halide, R—MgX which is commonly called Grignard reagents.

The Grignard reagents are obtained by the reaction of haloalkanes with magnesium metal in presence of dry ether.

$$CH_3CH_2Br + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}$$

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium, the magnesium halogen bond is essentially ionic.

$$\overset{\delta^-}{R} — \overset{\delta^+}{Mg}\,\overset{\delta^-}{X}$$

These are highly reactive and react with any source of proton to give hydrocarbons. Even alcohols, amines, water are sufficiently acidic to convert them to corresponding hydrocarbons.

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$

Due to its high reactivity, it is necessary to avoid even traces of moisture from a Grignard reagent.

On the other hand, this could be considered as one of the methods for converting halides to hydrocarbons.

(ii) Action with Sodium (Wurtz Reaction)

The reactions in which alkyl halides react with sodium in the presence of dry ether to form hydrocarbons containing double the number of carbon atoms present in the halide, are known as **Wurtz reaction.**

$$2RX + 2Na \xrightarrow{\text{Dry ether}} 2R + 2NaX$$

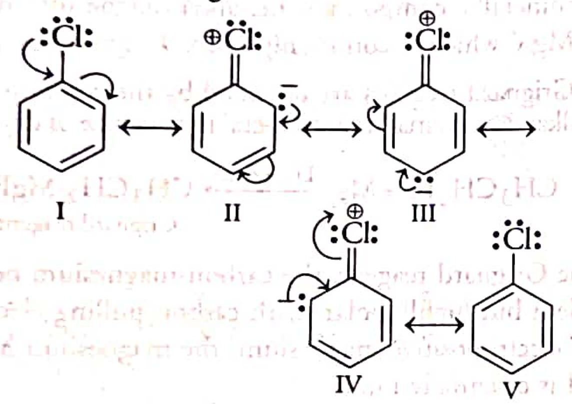
CHEMICAL REACTIONS OF HALOARENES

Some important chemical reactions of haloarenes are :

Nucleophilic Substitution Reactions

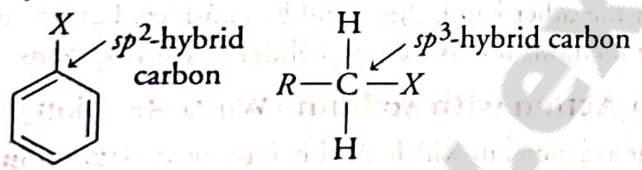
Nucleophilic substitution reactions in aryl halides occur only under drastic conditions. This is because haloarenes are chemically less reactive towards nucleophilic substitution reactions (than haloalkanes) due to the following reasons:

(i) **Resonance effect** In haloarenes like chlorobenzene, the lone pair of electrons on halogen atom are in conjugation with π-electrons of the ring and hence, these are delocalised on the benzene ring as shown below:



As a result of resonance, C—Cl bond acquires a partial double bond character. Thus, the bond cleavage in haloarene is difficult than haloalkane (where carbon is attached to halogen by a pure single bond) and thus, they are less reactive towards nucleophilic substitution reaction.

(ii) **Difference in hybridisation of carbon atom in C—*X* bond** In haloalkanes, the carbon atoms attached to halogen is sp^3-hybridised while in haloarenes, it is sp^2 hybridised.



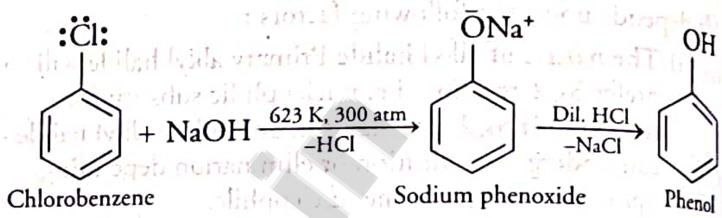
The sp^2 hybridised C-atom with greater *s*-character is more electronegative. It can hold the electron pair of the bond more tightly than the sp^3 hybridised C-atom with less *s*-character. As a result, the C—*X* bond in haloarenes (169 pm) is shorter than in haloalkanes (177 pm). Since, it is difficult to break a shorter (C—*X*) bond than a longer and therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

(iii) **Unstability of phenyl cation** In haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance, hence S_N1 mechanism cannot occur.

(iv) **Repulsion between the electron rich attacking nucleophiles and electron rich arenes** Because of electron rich arenes, electron rich nucleophile will not approach closely for the attack due to repulsion.

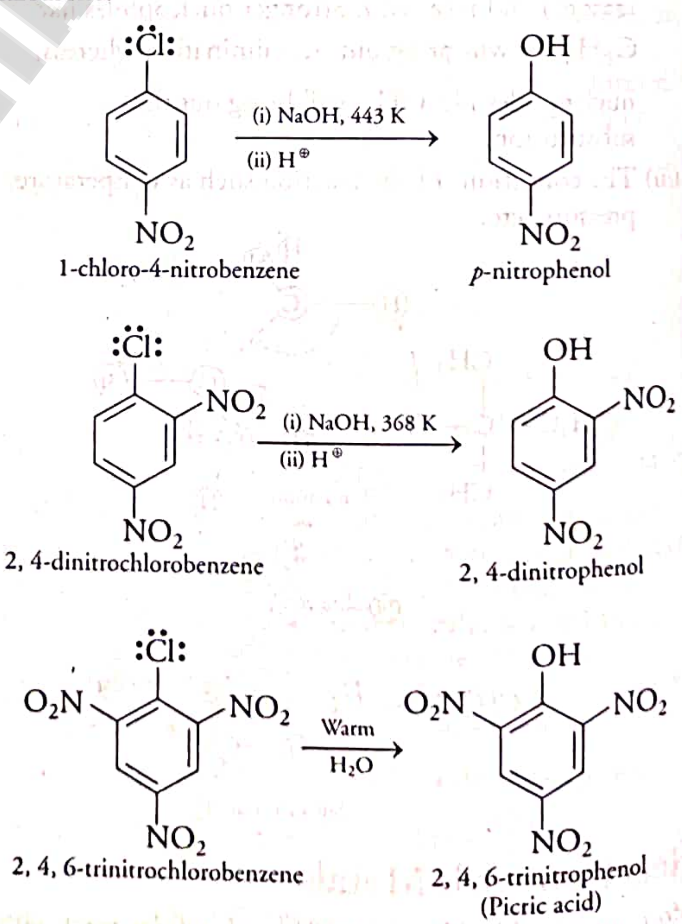
Replacement by Hydroxyl Group

Chlorobenzene when heated in *aq.* NaOH solution at a temperature of 623 K and a pressure of 300 atm, phenol is formed.



The presence of electron withdrawing groups such as $—NO_2$, —CN at *o*- and *p*-positions of haloarenes with respect to halogen, greatly activates the benzene ring towards nucleophilic substitution.

Further, greater the number of such groups at *o*-and *p*-positions with respect to halogen, more reactive is the haloarene.

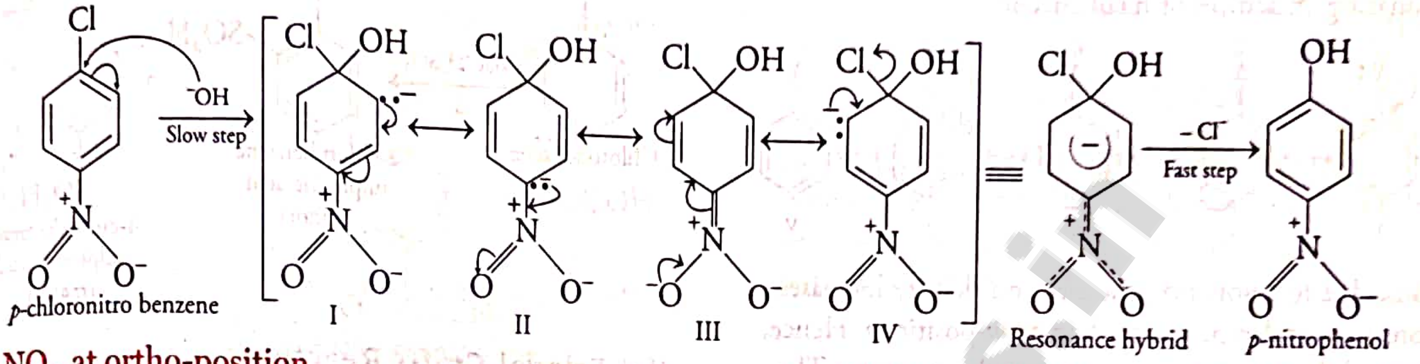


The $—NO_2$ group at *m*-position to the chlorine has no effect on reactivity.

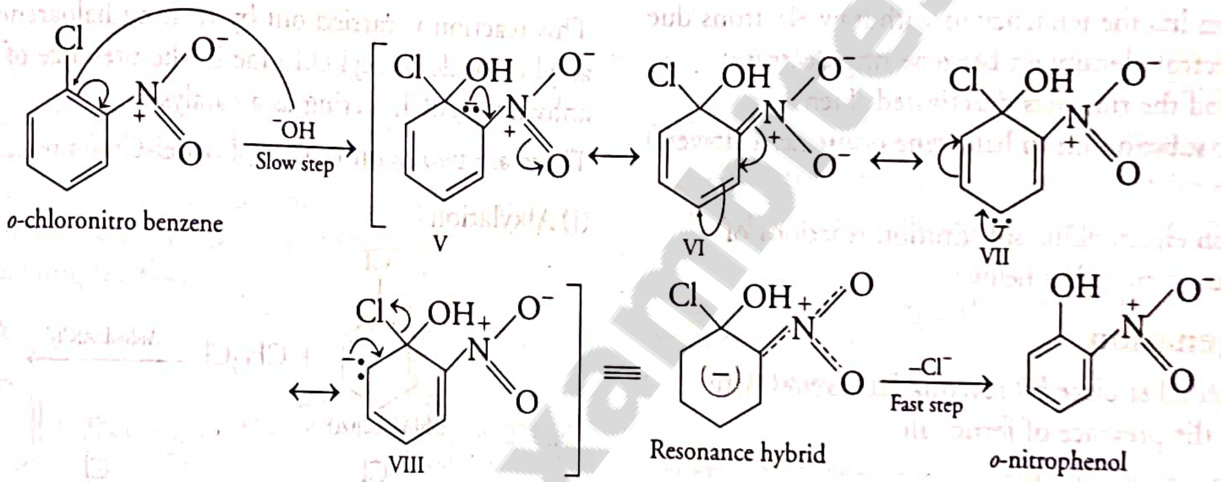
Mechanism

The presence of NO_2 groups at *o*- and *p*-positions withdraws electrons from benzene ring and facilitates the attack of nucleophile on haloarenes. The carbanion formed is stabilised through resonance as depicted below:

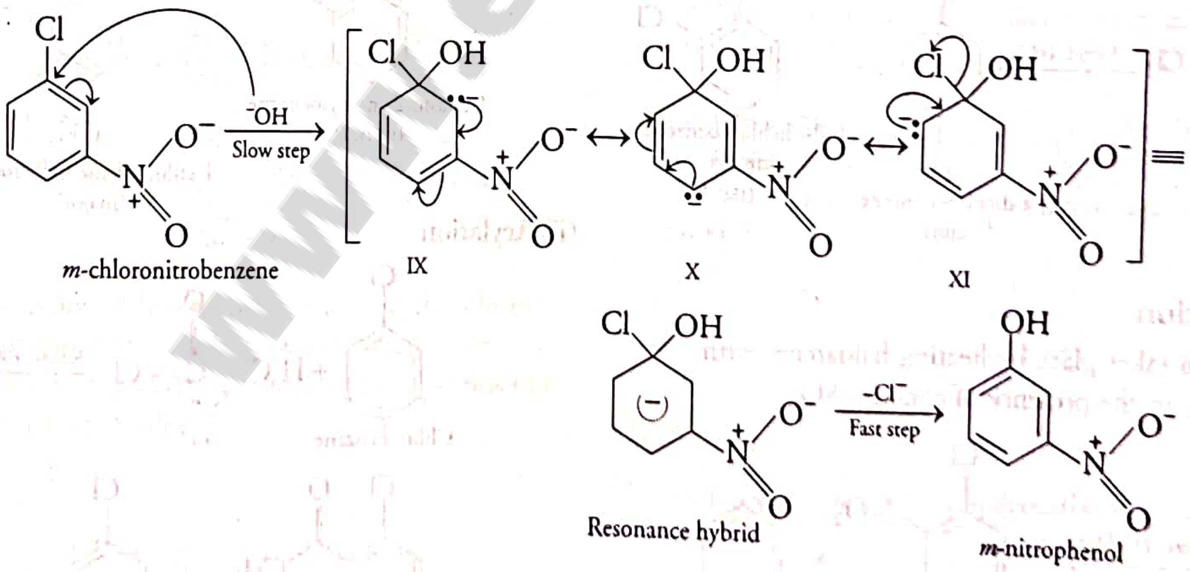
(i) NO_2 at para-position



(ii) NO_2 at ortho-position



(iii) NO_2 at meta-position

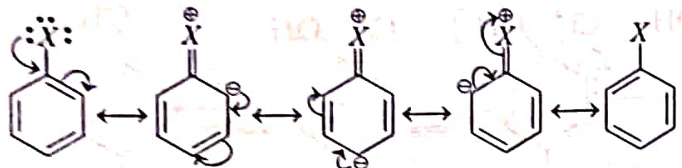


Note In the above structures showing NO_2 at *meta* position, there is no such structure in which the negative charge is present on carbon atom bearing the —NO_2 group. Therefore, the presence of nitro group at *meta* position does not stabilise the negative charge. Hence, no effect on reactivity is observed by the presence of —NO_2 group at *meta* position.

Electrophilic Substitution Reactions

Haloarenes undergo the usual electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reactions. In these reactions, stronger electrophile replaces weaker electrophile.The electrophilic

substitution reactions in haloarenes occur slowly and require more drastic conditions. This is due to the *ortho* and *para*-directing influence of halogen atom attached to a benzene ring which can be understood by the following resonating structures of halobenzene.



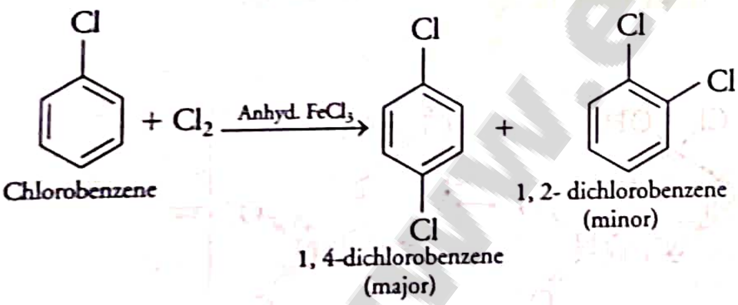
I II III IV V

Thus, due to resonance, the electron density increases more at *o*- and *p*-positions than at *m*-positions. Hence, electrophilic reactions occur at *o*- and *p*-position. The halogen atom has the tendency to withdraw electrons due to which electron density on benzene ring decreases (–*I*-effect) and the ring gets deactivated. Hence, electrophilic substitution in haloarene occurs at a slower rate.

The common electrophilic substitution reactions of haloarenes are depicted as below:

(i) Halogenation

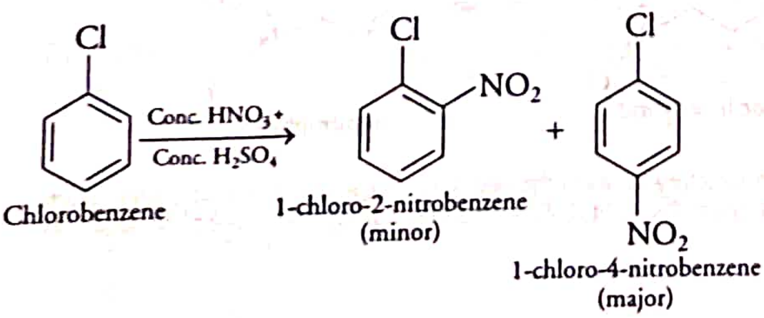
This reaction takes place by reacting haloarenes with halogens in the presence of ferric salt.



Chlorobenzene; 1, 4-dichlorobenzene (major); 1, 2- dichlorobenzene (minor)

(ii) Nitration

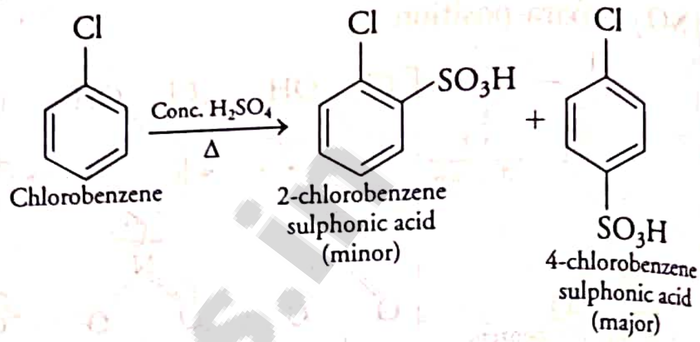
This reaction takes place by heating haloarenes with conc.HNO_3 in the presence of conc.H_2SO_4.



Chlorobenzene; 1-chloro-2-nitrobenzene (minor); 1-chloro-4-nitrobenzene (major)

(iii) Sulphonation

This reaction takes place by heating haloarenes with conc.H_2SO_4.



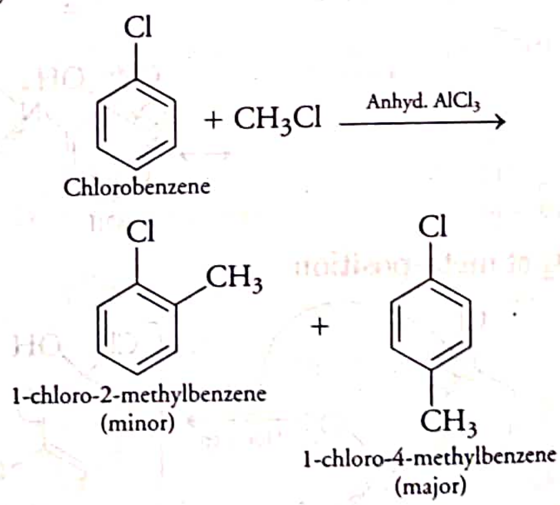
Chlorobenzene; 2-chlorobenzene sulphonic acid (minor); 4-chlorobenzene sulphonic acid (major)

(iv) Friedel-Crafts Reactions

This reaction is carried out by treating haloarenes with alkyl chloride or acyl chloride in the presence of anhydrous $AlCl_3$ acting as a catalyst.

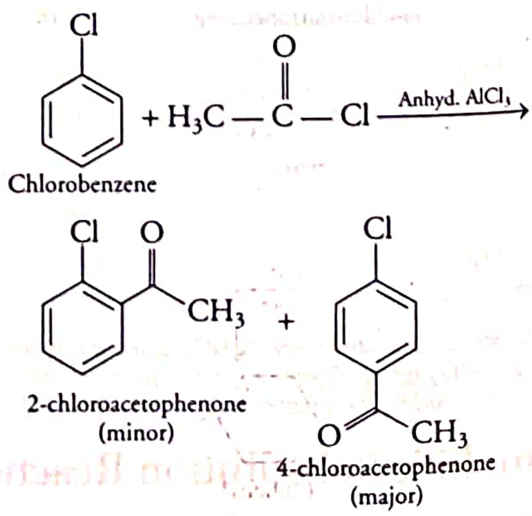
There are two main types of Friedel-Crafts reactions:

(i) Alkylation

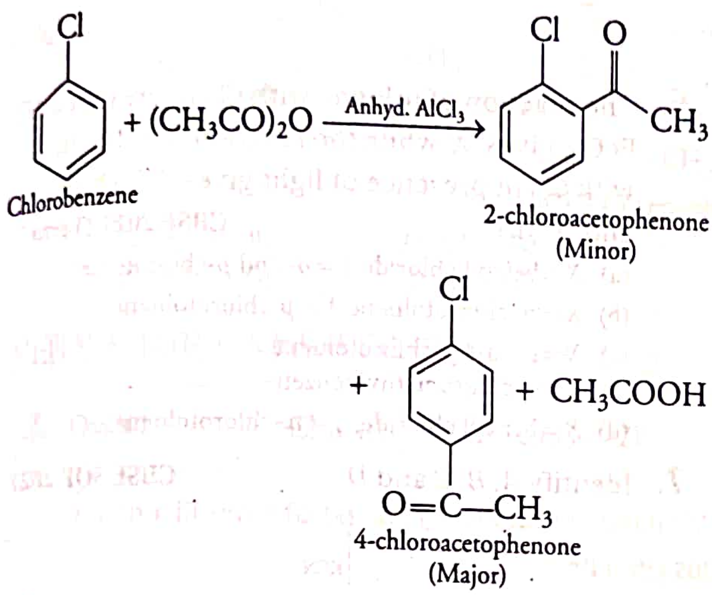


Chlorobenzene; 1-chloro-2-methylbenzene (minor); 1-chloro-4-methylbenzene (major)

(ii) Acylation

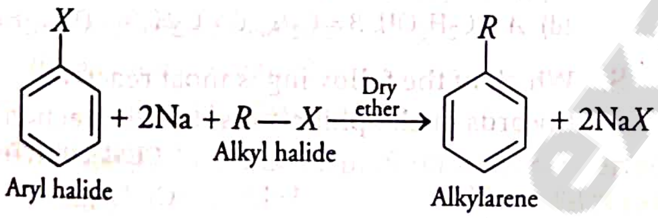


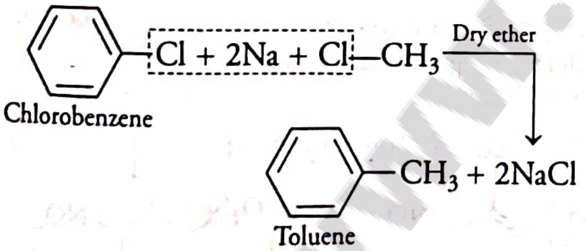
Chlorobenzene; 2-chloroacetophenone (minor); 4-chloroacetophenone (major)



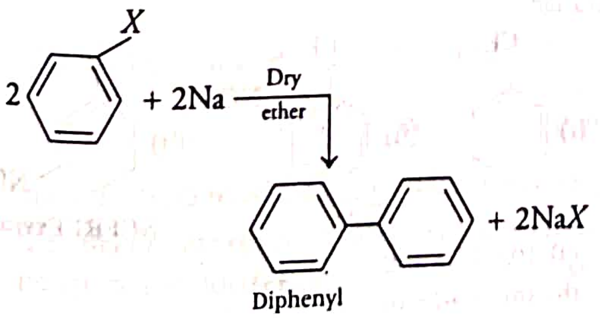
Reaction with Metals

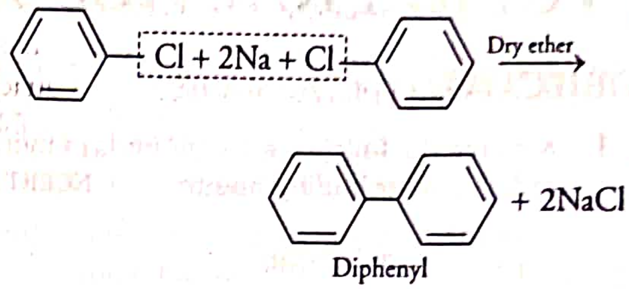
(i) **Wurtz-Fittig reaction** When aryl halide is heated with alkyl halide in the presence of sodium in dry ether, halogen atom is replaced by alkyl group and alkylarene is formed. This reaction is called Wurtz-Fittig reaction.



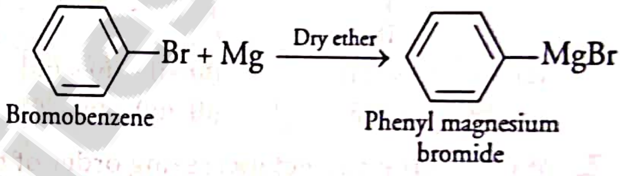


(ii) **Fittig reaction** When haloarenes react with sodium in the presence of dry ether, two aryl groups are joined together and diphenyl is formed. This reaction is called Fittig reaction.

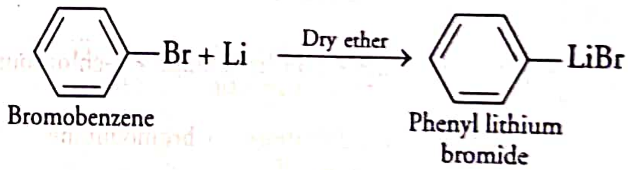




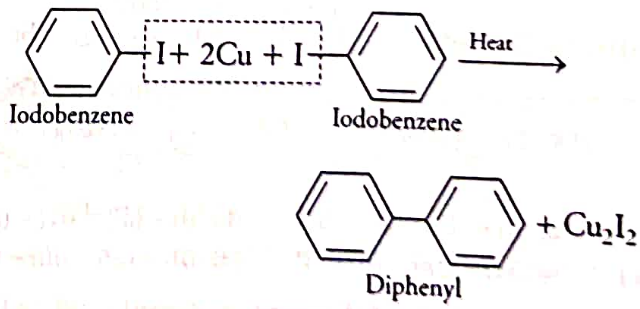
(iii) **Reaction with magnesium** Grignard reagent is formed. Like alkyl halides, aryl bromides and iodides also react with magnesium in dry ether to form Grignard reagent.



(iv) **Reaction with lithium** Bromo and iodoarenes react with lithium metal in the presence of dry ether to form their corresponding organometallic compounds.

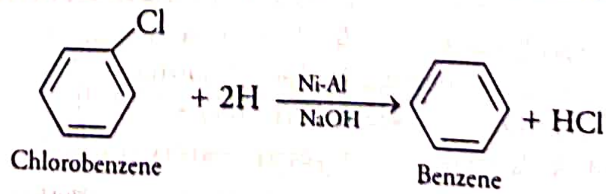


(v) **Reaction with copper powder** When iodobenzene is heated with copper powder in a sealed tube, diphenyl is formed. This reaction is called **Ullmann reaction.**



Reduction

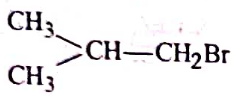
On reduction of haloarenes, hydrocarbons are formed.



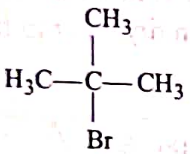
TOPIC PRACTICE 3

OBJECTIVE Type Questions

1. Arrange the following compounds in increasing order of their boiling points. **NCERT Exemplar**

(i) 

(ii) $CH_3CH_2CH_2CH_2Br$

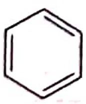
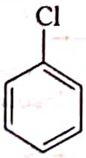
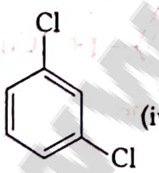
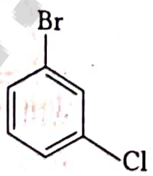
(iii) 

(a) (ii) < (i) < (iii) (b) (i) < (ii) < (iii)
(c) (iii) < (i) < (ii) (d) (iii) < (ii) < (i)

2. Which is the correct increasing order of boiling points of the following compounds?
1-iodobutane, 1-bromobutane, 1-chlorobutane, Butane **NCERT Exemplar**

(a) Butane < 1-chlorobutane < 1-bromobutane < 1-iodobutane
(b) 1-iodobutane < 1-bromobutane < 1-chlorobutane < Butane
(c) Butane < 1-iodobutane < 1-bromobutane < 1-chlorobutane
(d) Butane < 1-chlorobutane < 1-iodobutane < 1-bromobutane

3. Arrange the following compounds in the increasing order of their densities. **NCERT Exemplar**

(i)  (ii)  (iii)  (iv) 

(a) (i) < (ii) < (iii) < (iv) (b) (i) < (iii) < (iv) < (ii)
(c) (iv) < (iii) < (ii) < (i) (d) (ii) < (iv) < (iii) < (i)

4. Complete the following analogy:
Same molecular formula but different structures: *A* : : Non-superimposable mirror images : *B* **CBSE 2021 (Term I)**

(a) *A* : Isomers; *B* : Enantiomer
(b) *A* : Enantiomers; *B* : Racemic mixture
(c) *A* : Stereoisomers; *B* : Retention
(d) *A* : Isomers; *B* : Stereoisomers

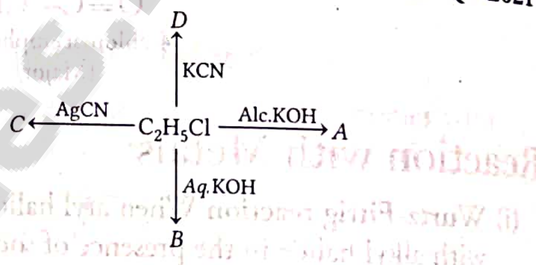
5. Which of the following alkyl halides will undergo S_N1 reaction most readily? **NCERT Exemplar**

(a) $(CH_3)_3C—F$ (b) $(CH_3)_3C—Cl$
(c) $(CH_3)_3C—Br$ (d) $(CH_3)_3C—I$

6. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives '*X*' while the reaction of toluene with Cl_2 in presence of light gives '*Y*'. Thus, '*X*' and '*Y*' are **CBSE 2021 (Term I)**

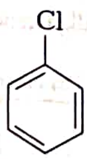
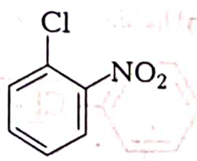
(a) X = benzyl chloride Y = *o*- and *p*-chlorotoluene
(b) X = *m*-chlorotoluene Y = *p*-chlorotoluene
(c) X = *o*- and *p*-chlorotoluene Y = trichloromethylbenzene
(d) X = benzyl chloride, Y = *m*-chlorotoluene

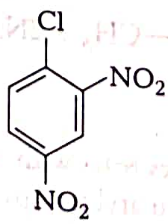
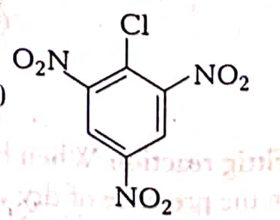
7. Identify *A*, *B*, *C* and *D* **CBSE SQP 2021**



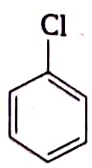
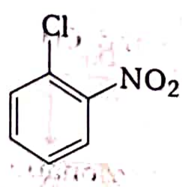
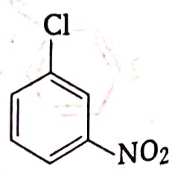
(a) $A = C_2H_4$, $B = C_2H_5OH$, $C = C_2H_5NC$, $D = C_2H_5CN$
(b) $A = C_2H_5OH$, $B = C_2H_4$, $C = C_2H_5CN$, $D = C_2H_5CN$
(c) $A = C_2H_4$, $B = C_2H_5OH$, $C = C_2H_5CN$, $D = C_2H_5NC$
(d) $A = C_2H_5OH$, $B = C_2H_4$, $C = C_2H_5NC$, $D = C_2H_5CN$

8. Which of the following is most reactive towards nucleophilic substitution reaction? **CBSE 2021 (Term I)**

(a)  (b) 

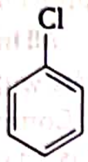
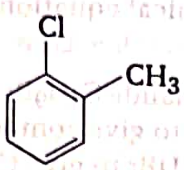
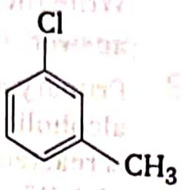
(c)  (d) 

Directions (Q. 9 and 10) *Arrange the given compounds in increasing order of rate of reaction towards nucleophilic substitution.*

9. (i)  (ii)  (iii) 

NCERT Exemplar

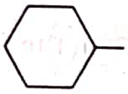
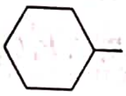
(a) (i) < (ii) < (iii)
(b) (iii) < (ii) < (i)
(c) (i) < (iii) < (ii)
(d) (iii) < (i) < (ii)

10. (i)  (ii)  (iii) 

NCERT Exemplar

(a) (i) < (ii) < (iii)
(b) (i) < (iii) < (ii)
(c) (iii) < (ii) < (i)
(d) (ii) < (iii) < (i)

VERY SHORT ANSWER Type Questions

11. Out of —Cl and —CH_2—Cl, which will react faster in S_N1 reaction with OH^-? **All India 2020**

12. Out of *o*- and *p*-dibromobenzene, which one has higher melting point and why? **NCERT Exemplar**

13. The following haloalkanes are hydrolysed in presence of *aq.* KOH. **CBSE SQP 2021**
    (i) 1- chlorobutane
    (ii) 2-chloro-2-methylpropane

    Which of the above is most likely to give
    (a) an inverted product?
    (b) a racemic mixture?

    Justify your answer.

14. How methyl bromide be preferentially converted to methyl isocyanide? **Delhi 2013 C**

15. Write the structure of an isomer of compound C_4H_9Br, which is most reactive towards S_N1 reaction? **All India 2016**

16. Out of $CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2Cl$ and $CH_3CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}Cl$, which one is more reactive towards S_N1 reaction and why? **Delhi 2016**

17. Which would undergo S_N2 reaction faster in the following pair and why?

$$CH_3{-}CH_2{-}Br \text{ and } CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}{-}CH_3$$

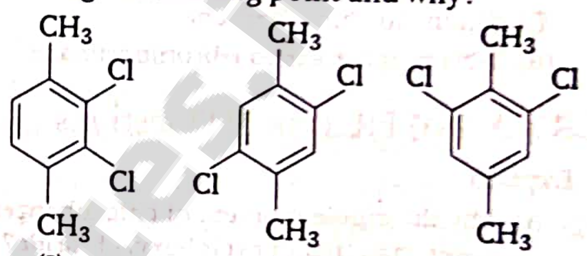
Delhi 2015

18. With the help of resonating structures explain the effect of presence of nitro group at *ortho* position in chlorobenzene. **CBSE SQP 2021**

SHORT ANSWER Type I Questions

19. Arrange each set of compounds in the order of increasing boiling points.
    (i) Bromomethane, bromoform, chloromethane, dibromomethane
    (ii) 1-chloropropane, *iso*-propyl chloride, 1-chlorobutane **NCERT Intext**

20. Which of the following compounds will have the highest melting point and why?



(I) (II) (III)

21. Write the mechanism of the following reaction:

$$nBuBr + KCN \xrightarrow{EtOH-H_2O} nBuCN$$

NCERT; Delhi 2011C

22. (i) Which alkyl halide from the following pair is chiral and undergoes faster towards S_N2 reaction?

(a)  (b) 

Delhi 2017

(ii) Out of S_N1 and S_N2, which reaction occurs with
(a) inversion of configuration?
(b) racemisation? **All India 2019, 2014**

23. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- and why?
    (i) CH_3Br or CH_3I
    (ii) $(CH_3)_3CCl$ or CH_3Cl **NCERT; Delhi 2014**

24. *Tert*-butylbromide reacts with *aq.* NaOH by S_N1 mechanism while *n*-butylbromide reacts by S_N2 mechanism. Why? **NCERT Exemplar**

25. Write the structure of the major organic product in each of the following reactions:
    (i) $(CH_3)_3CBr + KOH \xrightarrow[\text{Heat}]{\text{Ethanol}}$
    (ii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{Water}}$
    (iii) $CH_3CH_2Br + KCN \xrightarrow{aq.\ \text{ethanol}}$
    (iv) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

26. Elimination reactions (especially β-elimination) are as common as the nucleophilic substitution reaction in case of alkyl halides. Specify the reagents used in both cases.

27. The treatment of alkyl chlorides with aqueous KOH, leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain. **NCERT**

28. Carry out the following conversions in not more than 2 steps: **CBSE SQP 2021**
   (i) Aniline to chlorobenzene
   (ii) 2-bromopropane to 1-bromopropane

SHORT ANSWER Type II Questions

29. Explain
   (i) why the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
   (ii) why alkyl halides, though polar, are immiscible with water?

   Or

   why is the solubility of haloalkanes in water very low? **NCERT Exemplar**
   (iii) why Grignard reagents should be prepared under anhydrous conditions?
   Delhi 2013 C; Foreign 2012 ; NCERT

30. Following compounds are given to you:
   2-bromopentane, 2-bromo-2-methylbutane, 1-bromopentane
   (i) Write the compound which is most reactive towards S_N2 reaction.
   (ii) Write the compound which is optically active.
   (iii) Write the compound which is most reactive towards β-elimination reaction.
   Delhi 2017; All India 2017

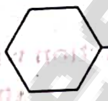
31. (i) Account for the following
   (a) Electrophilic substitution reactions in haloarenes occur slowly.
   (b) Haloalkanes, though polar, are insoluble in water.
   (ii) Arrange the following compounds in increasing order of reactivity towards S_N2 displacement:
   2-bromo-2-methylbutane, 1-bromopentane, 2-bromopentane **All India 2017 C**

32. What happens when
   (i) chlorobenzene is treated with $Cl_2/FeCl_3$?
   (ii) ethyl chloride is treated with $AgNO_2$?
   (iii) 2-bromopentane is treated with alcoholic KOH?

   Write the chemical equations in support of your answer. **All India 2015**

33. Primary alkyl halide C_4H_9Br (A) reacts with alcoholic KOH to give compound B. Compound B is reacted with HBr to give C, which is an isomer of A. When A is reacted with sodium metal, it gives compound D, C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of A and write the equations for all the reactions. **NCERT**

34. Identify A, B, C, P, Q, R and R' in the following:

   (i)  $-Br + Mg \xrightarrow{\text{Dry ether}} A \xrightarrow{H_2O} B$

   (ii) $R-Br + Mg \xrightarrow{\text{Dry ether}} C \xrightarrow{D_2O} \underset{\substack{|\\ D}}{CH_3CHCH_3}$

   (iii) $$\begin{array}{c} CH_3\ CH_3 \\ CH_3-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-CH_3 \\ CH_3\ CH_3 \end{array} \xleftarrow{Na/Ether} R'-X$$
   $$\xrightarrow{Mg} P \xrightarrow{H_2O} Q$$
   NCERT Intext

35. (i) Write the structural formula of A, B, C and D in the following sequence of reaction:

   $$\underset{}{CH_3-\overset{\overset{Cl}{|}}{CH}-CH_3} \xrightarrow[\text{KOH}]{\text{Alc.}} A \xrightarrow[\text{Peroxide}]{\text{HBr}} B \xrightarrow[\text{Dry ether}]{\text{NaI}} C$$
   $$B \xrightarrow[\text{Dry ether}]{\text{Mg}} D$$

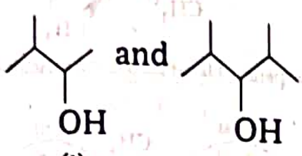
   (ii) Illustrate Sandmeyer's reaction with the help of a suitable example. **Delhi 2017**

36. Give reasons for the following.
   (i) Ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.
   (ii) (±) 2-butanol is optically inactive.
   (iii) C—X bond length in halobenzene is smaller than C—X bond length in CH_3-X. **All India 2013**

   Or The C— Cl bond length in chlorobenzene is shorter than that in CH_3Cl. **Delhi 2013**

37. Give reasons:
   (i) n-butyl bromide has higher boiling point than t-butyl bromide.
   (ii) Racemic mixture is optically inactive.
   (iii) The presence of nitro group $(-NO_2)$ at o/p positions, increases the reactivity of haloarenes towards nucleophilic substitution reactions. **Delhi 2015**

38. (a) Identify the chiral molecule in the following pair:



(i) (ii) **CBSE 2018**

(b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

(c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH.

LONG ANSWER Type Questions

39. How can the following conversions be carried out?
 (i) Ethyl chloride to propanoic acid
 (ii) Ethanol to propane nitrile
 (iii) 1-bromopropane to 2-bromopropane
 (iv) 2-chlorobutane to 3,4-dimethylhexane
 (v) 2-methyl-1-propene to 2-chloro-2-methylpropane **NCERT**

40. What happens when
 (i) *n*-butyl chloride is treated with alcoholic KOH?
 (ii) bromobenzene is treated with Mg in the presence of dry ether?
 (iii) chlorobenzene is subjected to hydrolysis?
 (iv) methyl bromide is treated with sodium in the presence of dry ether?
 (v) methyl chloride is treated with KCN? **NCERT**

41. How can the following conversions be carried out? **All India 2017**
 (i) 2-bromopropane to 1-bromopropane
 (ii) But-1-ene to *n*-butyl iodide
 (iii) 2-chloropropane to 1-propanol
 (iv) *iso*-propyl alcohol to iodoform
 (v) Chlorobenzene to *p*-nitrophenol **NCERT**

42. (i) Taking example of (–)2-methyl-1-butanol reacting with HCl, explain the process of inversion, retention and racemisation.
 (ii) Explain why both *dextro* and *laevo* forms of butan-2-ol are prepared in equal proportions, when S_N1 reaction of 2-chlorobutane is carried out in the presence of aqueous potassium hydroxide?

HINTS AND EXPLANATIONS

1. (*c*) Boiling point of a compound depends upon the surface area. Higher the surface area, higher will be the boiling point of a compound.
Thus, the increasing order of their boiling points

$$H_3C-\underset{Br}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 < \underset{\text{(Branching)}}{\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH-CH_2Br}$$

(Maximum branching;lowest b.p.346K)

$$< CH_3CH_2CH_2CH_2Br$$

(Straight chain; higher b.p.) 375K

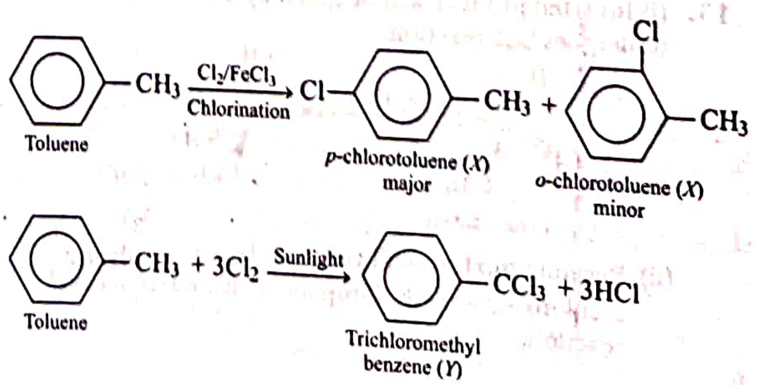
2. (*a*) Higher the surface area, higher will be the intermolecular forces of attraction and thus boiling point too. Boiling point increases with increase in molecular mass of halogen atom for the similar type of alkyl halide. Butane has no halogen atom and rest of all three compounds are halo derivatives of butane. Atomic mass of iodine is highest so the boiling point of 1-iodobutane is maximum among all the given compounds and hence, option (a) correct.

3. (*a*) Density is directly related to molecular mass. Higher the molecular mass, higher will be the density of the compound. Among the four given compounds, the order of molecular mass is
benzene < chlorobenzene < dichlorobenzene < bromochlorobenzene
Therefore, the increasing order of their densities are same as above.
Hence, option (a) is correct.

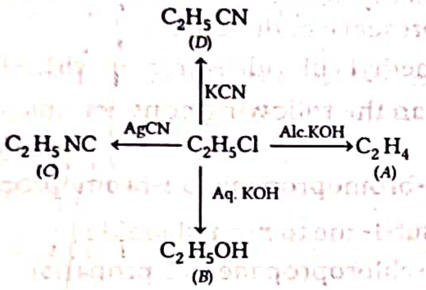
4. (*b*) Isomers are the compounds with same molecular formula but different structures.
Refer to text on pg 229.

5. (*d*) All the given compounds are tertiary alkyl halides but the bond formed between carbon and iodine (C — I) is the weakest bond due to large difference in the size of carbon and iodine. So, $(CH_3)_3C—I$ gives S_N1 reaction most readily. In other words, iodine is a better leaving group.

6. (*c*)



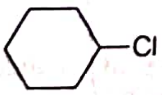
7. (*a*) Reactions given in flow chart (*D, C, B*) are nucleophilic substitution reactions. When a nucleophile stronger than the halide ion reacts with haloalkane having a partial positive charge on the carbon atom bonded to halogen, then substitution reaction takes place. Reaction (*A*) leads to elimination reaction.
Complete reactions are as follows:



8. (*d*)

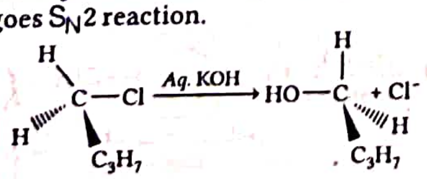
9. (*c*) The bond formed between C of benzene ring and halogen is more stable because of resonance it has partial double bond character. So, rate of reaction towards nucleophilic substitution is slow. This substitution is facilitated by the presence of electron withdrawing group at *ortho* and *para* position because electron density is high at these positions.
Compound (ii) and (iii) both have one electron withdrawing group but in compound (ii) electron withdrawing ($-NO_2$) group is present at *ortho* position, so rate of reaction in compound (ii) is more than that of compound (iii) while (i) has no electron withdrawing group.
Hence, the correct option is (c).

10. (*d*) Presence of electron releasing group at *ortho* or *para* position decreases the rate of nucleophilic substitution reaction. In compound (iii), electron releasing group is present at *meta* position *w.r.t.* chlorine, so the impact is less but in compound (ii) it is present at *ortho* position.
Thus, the rate of reaction towards nucleophilic substitution is least in compound (ii) and highest in compound (i) as there is no electron releasing group in this compound.

11. 

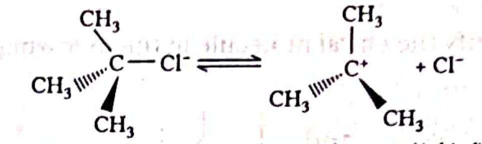
12. *p*-dibromobenzene has higher melting point than its *o*-isomer due to symmetry of *p*-isomer that fits in the crystal lattice better than the *o*-isomer. Hence, *p*-isomer has higher melting point than *o*-isomer (or *m*-isomer).

13. (i) Inverted product will be given by 1 chlorobutane as it undergoes S_N2 reaction.

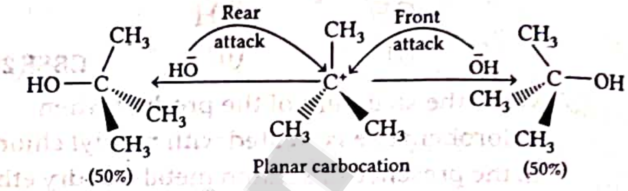


1-chlorobutane

(ii) Racemic mixture will be given by 2-chloro - 2 - methylpropane as it undergoes S_N1 reaction.



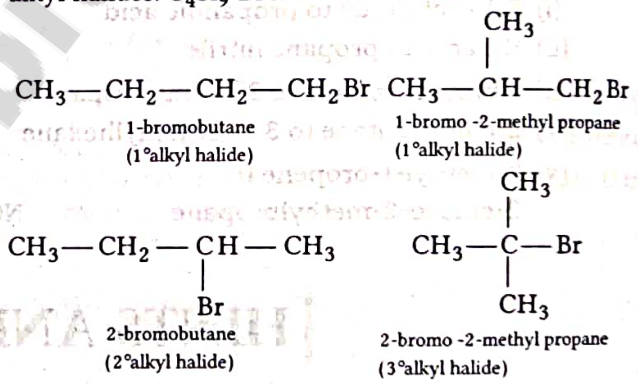
2-chloro-2-methylpropane Planar carbocation (Achiral)



14. It can be done by treating the methyl bromide with alcoholic silver cyanide.

$$\underset{}{CH_3Br} + \underset{\text{(Alc.)}}{AgCN} \longrightarrow \underset{\substack{\text{Methyl}\\\text{isocyanide}}}{CH_3NC} + AgBr$$

15. Tertiary (3°) alkyl halides are most reactive towards S_N1 reactions followed by secondary (2°) and primary (1°) alkyl halides. C_4H_9 Br has four isomers:



As 3° alkyl halides form a more stable 3° carbocation intermediate than secondary and primary alkyl halides which form 2° and 1° carbocation, respectively.

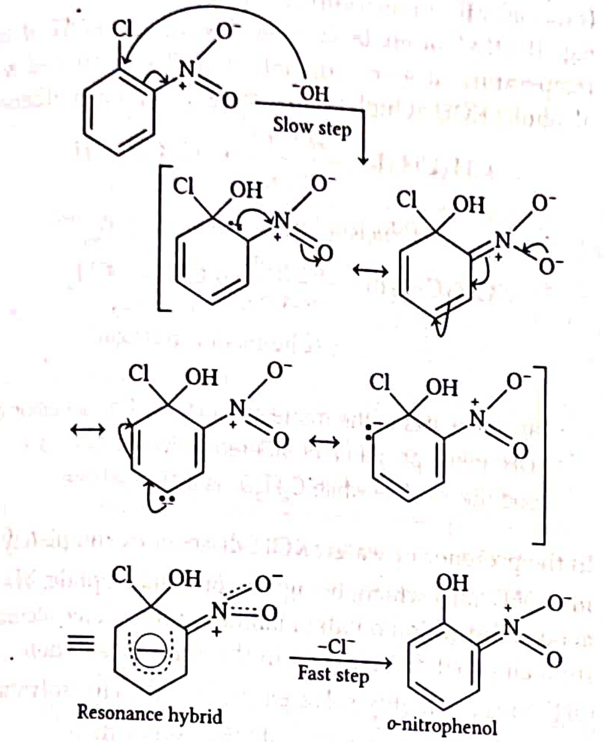
Hence, the isomer, $CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-Br$ (2-bromo-2-methyl propane) of compound C_4H_9 Br is most reactive towards S_N1 reactions.

16. $CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-Cl$ will undergo S_N1 reaction faster because it is a secondary alkyl halide and forms a secondary carbocation that can stabilise itself more than primary carbocation.

17. On steric hindrance grounds, 1° alkyl halides are more reactive than tert-alkyl halides in S_N2 reactions. Thus, CH_3-CH_2-Br reacts at a faster rate than $(CH_3)_3CBr$ in S_N2 reaction, because it is a primary halide, i.e. less hindered.

18. Nitro group at *ortho* position in chlorobenzene withdraws the electron density from the benzene ring and thus facilitates the attack of nucleophile on haloarene.

NO_2 at *ortho*-position



19. (i) For the same alkyl group, boiling point increases with the size of the halogen atom. Thus, boiling point of bromomethane is higher than that of chloromethane. Further, the boiling point increases as the number of halogen atoms increases. Thus, the boiling point of bromoform with three Br atoms is highest followed by dibromomethane with two Br atoms while that of bromomethane containing only one Br atom is lowest. Therefore, the arrangement of the given compounds in the order of increasing boiling points is as follows:

CH_3Cl (chloromethane) < CH_3Br (bromomethane) < CH_2Br_2 (dibromomethane) < $CHBr_3$(bromoform).

(ii) For the same halogen, boiling point increases with an increase in the size of the alkyl group. Thus, the boiling point of 1-chlorobutane is higher than those of 1-chloropropane and isopropyl chloride. Further, the boiling point decreases as the branching increases. Thus, the boiling point of chloropropane is higher than isopropyl chloride.

Therefore, the arrangement of the given compounds in the order of increasing boiling points is as follows:

$(CH_3)_2$ CHCl (*iso*-propyl chloride or 2-chloropropane) < $ClCH_2CH_2CH_3$ (1-chloropropane) < $ClCH_2CH_2CH_2CH_3$ (1-chlorobutane).

20. Compound (II) is most symmetrical because it has both the CH_3 groups and Cl atoms *p* – to each other. Therefore, it fits in the crystal lattice better than the other two isomers and hence it has the higher melting point.

21.

> (i) Write the resonating structures of KCN.
> (ii) Due to the presence of polar solvent, find the possibility that which product will be formed preferentially.

KCN gives CN^- ion as a nucleophile in aqueous medium.

Resonating forms of KCN are:

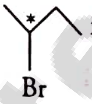
$$\overset{+}{K}[\overset{-}{:C}\equiv N:] \longleftrightarrow [:C=\ddot{N}\overset{-}{:}]K^+$$

Thus, cyanide ion is an ambident nucleophile. Therefore, it can attack the C-atom of C—Br bond in *n*-BuBr either through C-atom or through N-atom. Thus, two possible products are cyanides and isocyanides, respectively.

But C—C bond is more stable than C—N bond, so attack occurs through C-atom and hence, cyanide is predominantly formed.

$$\overset{+}{K}\overset{-}{CN} + \underbrace{CH_3—CH_2—CH_2—\overset{\delta+}{CH_2}—\overset{\delta-}{Br}}_{n\text{-butyl bromide}} \longrightarrow$$

$$\underbrace{CH_3—CH_2—CH_2—CH_2C\equiv N}_{n\text{-butyl cyanide}} + \overset{-}{Br}$$

22. (i) (a)  is chiral.

(b)  undergoes faster towards S_N2 reaction as it is a primary halide.

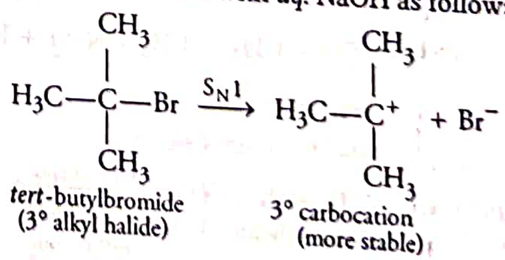
(ii) (a) S_N2 reaction occurs with inversion of configuration.

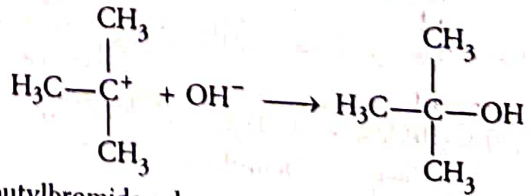
(b) S_N1 reaction proceeds with racemisation.

23. (i) CH_3Br and CH_3I both are primary halogen compounds. The reactivity will depend upon the size of the halogen atom. Iodine is a better leaving group because of larger size, therefore, CH_3I will react faster than CH_3Br.

(ii) Out of $(CH_3)_3CCl$ and CH_3Cl, the molecule being a primary halide, i.e. CH_3Cl, will react faster with OH^- because in S_N2 reaction, 1° halide reacts faster than 3° halide.

24. *Tert*-butylbromide reacts with *aq.* NaOH as follows:



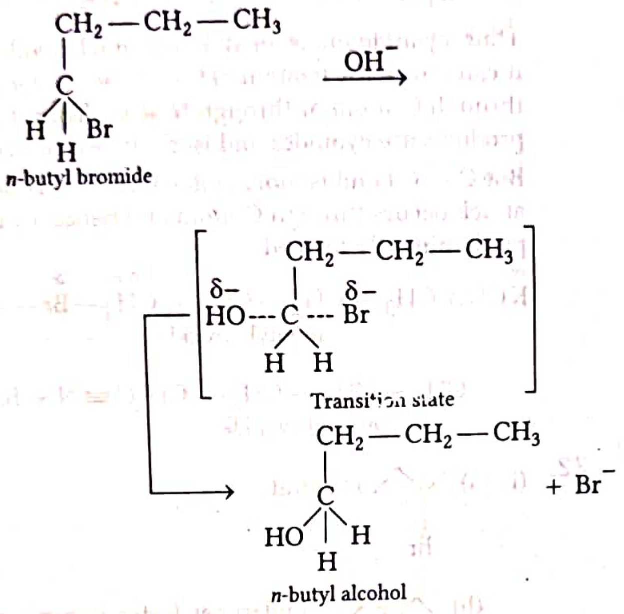


tert-butylbromide when treated with aqueous NaOH, it forms *tert*-carbocation which is more stable intermediate. This intermediate is further attacked by OH^- ion.

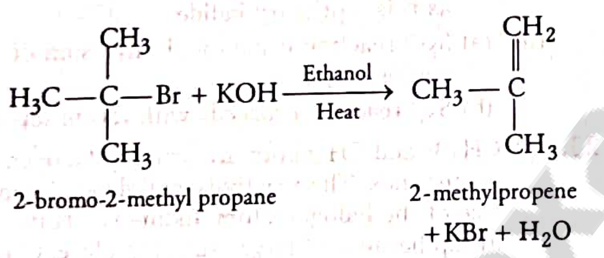
As *tert*-carbocation is highly stable, so *tert*-butylbromide follows S_N1 mechanism.

In case of *n*-butylbromide, primary carbocation is formed which is least stable, so it does not follow S_N1 mechanism. Here, steric hindrance is very less, so it

follows S_N2 mechanism. In S_N2 mechanism, OH^- will attack from backside and a transition state is formed.



25. (i)



(ii) $H_3C-\underset{\substack{| \\ Br}}{CH}-CH_2-CH_3 + NaOH \xrightarrow[\text{hydrolysis}]{\text{Water}}$

2-bromobutane

$CH_3-\underset{\substack{| \\ OH}}{CH}-CH_2-CH_3 + NaBr + H_2O$

2-butanol or butan-2-ol

(iii) $CH_3-CH_2-Br + KCN \xrightarrow[\text{(nucleophilic substitution)}]{aq.\ \text{ethanol}}$
Bromoethane

$CH_3-CH_2-C{\equiv}N + KBr$
Ethyl cyanide

(iv) $C_6H_5ONa + C_2H_5Cl \xrightarrow[\text{synthesis}]{\text{Williamson's}}$
Sodium phenoxide, Chloroethane

$C_6H_5-O-C_2H_5 + NaCl$
Ethyl phenyl ether

26. Elimination reactions are as common as the nucleophilic substitution reaction in case of alkyl halides as two reactions occur simultaneously. Generally, at lower temperature and by using weaker base, nucleophilic substitution reactions occur while at higher temperature and by using a stronger base, elimination reactions (especially β-elimination) take place.

e.g. If ethyl bromide is treated with *aq.* KOH at low temperature, it gives ethanol while if it is treated with alcoholic KOH at high temperature then it gives ethene.

$$\underset{}{CH_3CH_2Br} \xrightarrow[373\ K]{aq.\ KOH} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

(Nucleophilic substitution reaction)

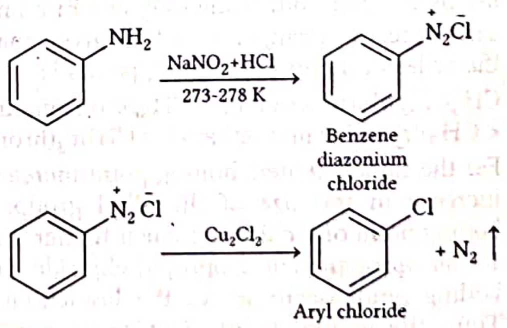
$$CH_3CH_2Br \xrightarrow[473\text{-}523\ K]{\text{Alc. KOH}} \underset{\text{Ethene}}{CH_2{=}CH_2}$$

(Elimination reaction)

27. > Difference lies in the mode and extent of dissociation of KOH in the presence of different solvents. OH^- is a good nucleophile while $C_2H_5O^-$ is a strong base.

In the presence of water, KOH dissociates completely into OH^- ions which, being a strong nucleophile, brings about substitution on alkyl halides and produce alcohols from alkyl halides. Further, in the aqueous solution, OH^- ions are highly solvated (hydrated). This solvation reduces the basic character of OH^- ions which therefore, fails to abstract a H-atom from the β-carbon of the alkyl chloride to form an alkene. In alcoholic medium, solution also contains $C_2H_5O^-$, ethoxide ions in addition to OH^- ions. Being a stronger base than OH^-, they abstract H^+ ion from β-C-atom, giving rise to an alkene as a major product (dehydrohalogenation).

28. (i)

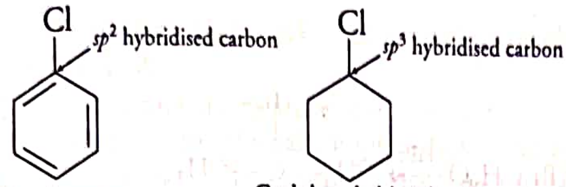


(ii) $\underset{\text{2-bromopropane}}{CH_3\overset{\substack{Br \\ |}}{CH}-CH_3} \xrightarrow{\text{Alc. KOH}} \underset{\text{Propene}}{CH_3-CH{=}CH_2} + HBr$

$\downarrow$ HBr/Peroxide

$\underset{\text{1-bromopropane}}{CH_3CH_2CH_2Br}$

29. > (i) Find the hybridisation of C-atoms in chlorobenzene and cyclohexyl chloride and electronegativity to find the bond polarity and thus, dipole moment.
> (ii) Strong intermolecular H-bonding exist among water molecules.
> (iii) Consider the reactive nature of Grignard reagents with water.

(i) 

Chlorobenzene   Cyclohexyl chloride

Due to sp^2 hybridisation of C-atom in chlorobenzene, C-atom is more electronegative (greater *s*-character) whereas in cyclohexyl chloride, C-atom is sp^3 hybridised, i.e. less electronegative (lesser *s*-character). So, polarity of C—Cl bond in chlorobenzene is less than the C—Cl bond in cyclohexyl chloride. Further, due to delocalisation of lone pair of electrons of Cl-atom over the benzene ring, C—Cl bond in chlorobenzene acquires some double bond character while C—Cl bond in cyclohexyl chloride is a pure single bond. Thus, C—Cl bond in chlorobenzene is shorter than in cyclohexyl chloride. As dipole moment is a product of charge and distance, therefore, the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(ii) Water molecules have enough strong intermolecular H-bonding which is difficult to be broken by alkyl halides, though they are polar in nature as well. Therefore, alkyl halides do not dissolve in water and form separate layers.

(iii) Grignard reagents ($R—Mg—X$) are readily decomposed by water to produce alkanes. That is why, they should be prepared under anhydrous conditions. Instead, ether is used as a solvent during the preparation of Grignard reagent.

$$R—Mg—X + H_2O \longrightarrow \underset{\text{Alkane}}{R—H} + Mg\begin{matrix} X \\ OH \end{matrix}$$

30. (i) S_N2 reactions involve the formation of transition state. Higher the steric hinderance, lesser the stability of transition state and lower is their reactivity towards S_N2.

$$\underset{\substack{\text{1-bromopentane} \\ (1°)}}{CH_3CH_2CH_2CH_2CH_2Br} > \underset{\substack{\text{2-bromopentane} \\ (2°)}}{CH_3\underset{\substack{| \\ Br}}{C}HCH_2CH_2CH_3} > \underset{\substack{\text{2-bromo-2-methylbutane} \\ (3°)}}{CH_3\overset{\substack{Br \\ |}}{\underset{\substack{| \\ CH_3}}{C}}CH_2CH_3}$$

(ii) Among the given compounds, 2-bromopentane is optically active due to the presence of chiral carbon (*)

$$C_3H_7—\overset{\substack{H \\ |}}{\underset{\substack{| \\ Br}}{\overset{*}{C}}}—CH_3$$

Note A chiral carbon have four different groups or atoms attached separately to its four valencies.

(iii) 2-bromo-2-methylbutane is most reactive towards β-elimination reaction because in this case, more substituted alkene is the major product.

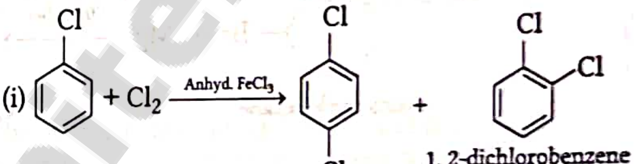
$$CH_3CH_2\overset{\substack{CH_3 \\ |}}{\underset{\substack{| \\ Br}}{C}}—CH_3 \xrightarrow[-HBr]{} \underset{\text{2-methyl but-2-ene}}{CH_3CH{=}\overset{\substack{CH_3 \\ |}}{C}—CH_3}$$

31. (i) (a) Refer to text on pages 233-234.

(b) Refer to text on pages 225

(ii) The correct increasing order of reactivity towards S_N2 displacement is

2-bromo-2-methylbutane < 2-bromopentane < 1-bromopentane

32. (i) 

1, 4-dichlorobenzene (Major)   1, 2-dichlorobenzene (Minor)

(ii) $CH_3CH_2Cl + AgNO_2 \longrightarrow CH_3CH_2NO_2 + AgCl$

(iii) When 2-bromopentane is treated with alcoholic KOH, it undergoes dehydrohalogenation leading to the formation of two or more different products depending upon the number of different types of β-hydrogen available.

The more highly substituted alkene (i.e. having lesser number of hydrogen atoms on the doubly bonded carbon atoms) is the major product of dehydrohalogenation. This is in accordance to Saytzeff rule.

$$\underset{\text{2-bromopentane (has 2 β-H-atoms)}}{\overset{\substack{H \\ |}}{C}H_2—\overset{\substack{Br \\ |}}{C}H—\overset{\substack{H \\ |}}{C}H—CH_2—CH_3} \xrightarrow{\text{alc.KOH}}$$

$$\underset{\text{pent-2-ene (Major)}}{CH_3—CH{=}CH—CH_2—CH_3} +$$

$$\underset{\text{Pent-1-ene (Minor)}}{CH_2{=}CH—CH_2—CH_2CH_3}$$

33. Two possible isomers of given primary alkyl halide, C_4H_9Br are:

$$\underset{\substack{[I] \\ (1°)}}{CH_3—CH_2—CH_2—CH_2—Br}; \quad \underset{\substack{[II] \\ (1°)}}{CH_3—\underset{\substack{| \\ CH_3}}{C}H—CH_2Br}$$

According to the question, compound *A* on reaction with sodium does not give the same product produced by *n*-butyl bromide. So, *A* cannot be [I].

$$\underset{n\text{-butyl bromide}}{2CH_3—CH_2—CH_2—CH_2—Br} + 2Na \xrightarrow{\text{Ether}}$$

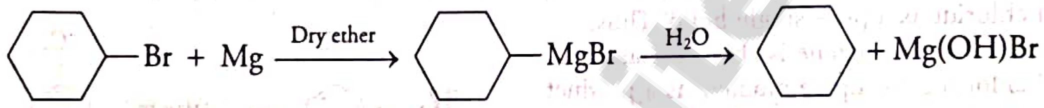
$$\underset{n\text{-octane (not formed in the reaction) } C_8H_{18}}{CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3}$$

Now, [II] must be the correct isomer.
Hence, the overall equations for all the reactions are:

$$\underset{\substack{iso\text{-butyl bromide}\\ \text{(1-bromo-2-methyl propane)}\\ (A)}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Br} \xrightarrow{\text{KOH(alc.)}} \underset{\substack{\text{2-methyl propene}\\ (B)}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2} + KBr + H_2O \xrightarrow{HBr} \underset{\substack{\text{2-bromo-2-methyl}\\ \text{propane}\\ (C)}}{CH_3-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3}$$

$$2\underset{(A)}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Br} + 2Na \xrightarrow[\text{Wurtz reaction}]{\text{Dry ether}} \underset{\substack{\text{2, 5-dimethyl hexane}\\ C_8H_{18}\,(D)}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3}$$

34. (i) Haloalkanes react with Mg in dry ether to form Grignard reagents ($RMgX$), which react with water to form hydrocarbons.



Bromocyclohexane — Cyclohexyl magnesium bromide [A] (Grignard reagent) — Cyclohexane [B]

(ii) In this reaction, R is $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$ group.

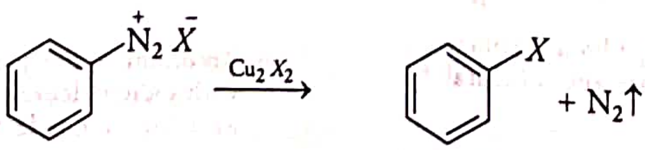
$$\underset{iso\text{-propyl bromide}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-Br} + Mg \xrightarrow{\text{Dry ether}} \underset{\substack{iso\text{-propyl magnesium}\\ \text{bromide } [C]\\ \text{(Grignard reagent)}}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-MgBr} \xrightarrow{D_2O} \underset{\text{2-deuteropropane}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-D} + Mg(OD)Br$$

(iii) Haloalkanes react with Na in dry ether to give hydrocarbons containing double number of C-atoms.

$$\underset{\text{2,2,3,3- tetramethylbutane}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3} \xleftarrow[\substack{\text{Wurtz}\\ \text{reaction}}]{\text{Na/dry ether}} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-X \xrightarrow{Mg} \underset{\substack{\text{Grignard reagent}\\ [P]}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-MgX} \xrightarrow{H_2O} \underset{\substack{\text{2-methylpropane}\\ [Q]}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-H} + Mg(OH)X$$

35. (i) $$CH_3-\overset{\displaystyle Cl}{\overset{|}{CH}}-CH_3 \xrightarrow[\text{KOH}]{\text{alc.}} \underset{(A)}{CH_3-CH=CH_2} \xrightarrow[\text{peroxide}]{HBr} \underset{(B)}{CH_3CH_2CH_2Br} \xrightarrow[\text{dry ether}]{NaI} \underset{(C)}{CH_3CH_2CH_2I} \xrightarrow[\text{dry ether}]{Mg} \underset{(D)}{CH_3CH_2CH_2MgI}$$

(ii) Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide, results in the replacement of the diazonium group by —Cl or —Br.



Aryl halide

(X = Cl, Br)

36. (i) Iodide is a better leaving group because of its larger size than bromide, therefore, ethyl iodide undergoes S_N2 reaction faster than ethyl bromide.

(ii) (±) 2-butanol is a racemic mixture. It is a mixture which contains two enantiomers in equal proportion and thus, have zero optical rotation due to internal compensation. Therefore, it is optically inactive.

(iii) In halobenzenes (like chlorobenzene), the lone pair of electrons on halogen atom is delocalised on the benzene ring. As a result, C — *X* bond (C — Cl bond in case of chlorobenzene) acquires some double bond character while in $CH_3—X$, C—*X* bond is a pure single bond. Therefore, C—*X* bond in halobenzene is shorter than in $CH_3—X$.

37. (i) For isomeric alkyl halides, the boiling points decreases with branching because with branching, the surface area of the alkyl halide decreases and hence, the magnitude of van der Waals' forces of attraction decreases. Therefore, *n*-butyl bromide ($CH_3CH_2CH_2CH_2Br$) has higher boiling than *tert*-butyl bromide,

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Br$$

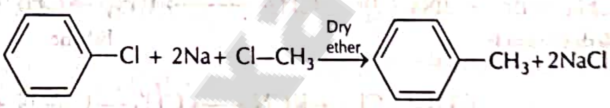
(ii) Racemic mixture contains two enantiomers, i.e. *d*- and *l*- forms in equal proportions and possesses zero optical rotation as the rotation of plane polarised light due to one isomer will be cancelled by the rotation due to the other isomer. Thus, the mixture will be optically inactive.

(iii) Refer to text on page 232 and 233.

38. (a) A molecule which completely lacks symmetry is called chiral. The mirror images of such molecules are non-superimposable. Molecule (*i*) is chiral in given structures as the mirror images are non-superimposable.

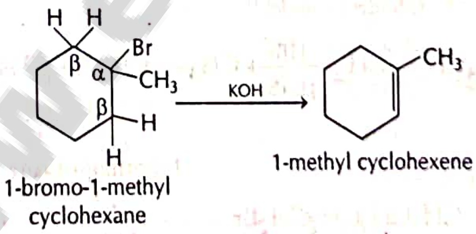
Mirror image

(b) It is Wurtz-Fittig reaction.



Toluene

(c)



β-hydrogen on each side of Br atom are equivalent, because of which only one alkene will be formed.

39. (i) $\underset{\text{Ethyl chloride (Chloroethane)}}{CH_3—CH_2—Cl} \xrightarrow{KCN} \underset{\text{Ethyl nitrile (Cyanopropane)}}{CH_3—CH_2—C\equiv N} \xrightarrow{2H_2O/H^+} \underset{\text{Propanoic acid}}{CH_3—CH_2—COOH}$

(ii) $\underset{\text{Ethanol}}{CH_3—CH_2—OH} \xrightarrow{\text{Red P/I}_2} \underset{\text{Iodoethane}}{CH_3—CH_2—I} \xrightarrow{KCN} \underset{\text{Propane nitrile}}{CH_3—CH_2—CN}$

(iii) $\underset{\text{1-bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\Delta]{\text{KOH (alc.)}} \underset{\text{Prop-1-ene}}{CH_3CH=CH_2} \xrightarrow{HBr} \underset{\text{2-bromopropane}}{CH_3\underset{\underset{\displaystyle Br}{|}}{C}H—CH_3}$

(iv) $\underset{\text{2-chlorobutane}}{2CH_3—CH_2—\underset{\underset{\displaystyle CH_3}{|}}{C}H—Cl} + 2Na \xrightarrow[\text{Wurtz reaction}]{\text{Dry ether}} \underset{\text{3, 4-dimethylhexane}}{CH_3—CH_2—\underset{\underset{\displaystyle CH_3}{|}}{C}H—\underset{\underset{\displaystyle CH_3}{|}}{C}H—CH_2—CH_3} + 2NaCl$

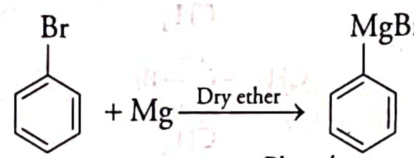
(v) $CH_3-\underset{\substack{|\\ CH_3}}{C}=CH_2 \xrightarrow{HCl} CH_3-\overset{\substack{Cl\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-CH_3$

2-methyl-1-propene → 2-chloro-2-methylpropane

40. (i) But-1-ene is formed as a result of dehydrohalogenation.

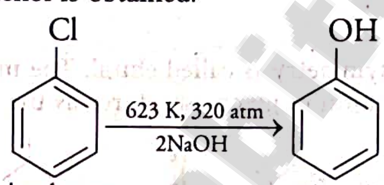
$$\underset{n\text{-butyl chloride}}{CH_3-CH_2-CH_2-CH_2-Cl} + \underset{(Alc.)}{KOH} \longrightarrow \underset{\text{But-1-ene}}{CH_3-CH_2-CH=CH_2} + KCl + H_2O$$

(ii) Phenyl magnesium bromide is formed.



Bromobenzene + Mg —Dry ether→ Phenyl magnesium bromide (Grignard reagent)

(iii) At room temperature and pressure, no reaction occurs but when chlorobenzene is heated with 6-8 % NaOH solution at 623K under 320 atmospheric pressure, phenol is obtained.



Chlorobenzene —623 K, 320 atm, 2NaOH→ Phenol

(iv) Ethane is formed as a result of Wurtz reaction.

$$\underset{\text{Methyl bromide}}{CH_3-Br} + 2Na + Br-CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaBr$$

(v) Cyanomethane is formed.

$$\underset{\substack{\text{Chloromethane}\\ \text{(Methyl chloride)}}}{CH_3-Cl} + KCN \longrightarrow \underset{\text{Acetonitrile}}{CH_3-C\equiv N} + KCl$$

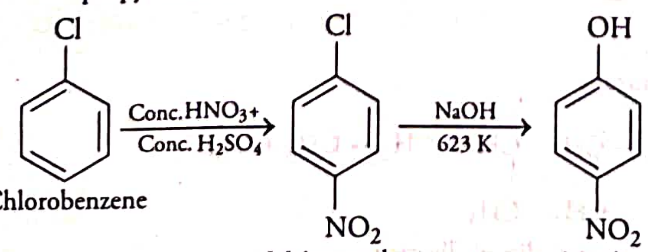
41. (i) $\underset{\text{2-bromopropane}}{CH_3-\underset{\substack{|\\ Br}}{CH}-CH_3} \xrightarrow{\text{Alc. KOH}} CH_3CH=CH_2 \xrightarrow[H_2O_2]{HBr} \underset{\text{1-bromopropane}}{CH_3-CH_2-\underset{\substack{|\\ Br}}{CH_2}}$

(ii) $\underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} \xrightarrow[\text{Peroxide}]{HBr} \underset{n\text{-butyl bromide}}{CH_3CH_2CH_2CH_2Br} \xrightarrow[\substack{\text{Acetone}\\ \text{(Finkelstein reaction)}}]{NaI} \underset{n\text{-butyl iodide}}{CH_3CH_2CH_2CH_2I}$

(iii) $\underset{\text{2-chloropropane}}{CH_3-\underset{\substack{|\\ Cl}}{CH}-CH_3} \xrightarrow[\Delta]{KOH(alc.)} \underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[\substack{\text{Anti-Markovnikov's}\\ \text{addition}}]{\text{HBr, Peroxide}} \underset{\text{1-bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\substack{\text{Nucleophilic}\\ \text{substitution}}]{KOH(aq),\ \Delta} \underset{\text{Propanol}}{CH_3CH_2CH_2OH}$

(iv) $\underset{iso\text{-propyl alcohol}}{CH_3-\underset{\substack{|\\ OH}}{CH}-CH_3} + 4I_2 + 6NaOH \xrightarrow[\substack{\text{(Iodoform}\\ \text{reaction)}}]{\text{Heat}} \underset{\text{Iodoform}}{CHI_3}\downarrow + \underset{\text{Sodium ethanoate}}{CH_3COONa} + 5NaI + 5H_2O$

(v)



Chlorobenzene —Conc. HNO_3 + Conc. H_2SO_4→ Major product —NaOH, 623 K→ p-nitrophenol

42. (i) Refer to text on pages 229-230. (ii) Refer to text on page 230.

|TOPIC 4| Polyhalogen Compounds

Carbon compounds having more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture. Some important polyhalogen compounds are described as follows:

DICHLOROMETHANE

(Methylene Chloride, CH_2Cl_2)

It is colourless, sweet smelling volatile liquid, having low boiling point of 313 K and specific gravity of 1.37. It is prepared industrially by the direct chlorination of methane in the presence of diffused sunlight.

$$CH_4 + 2Cl_2 \xrightarrow{h\nu} CH_2Cl_2 + 2HCl$$

Uses

It is used

(i) as a solvent and also as a paint remover.
(ii) as a propellant in aerosols.
(iii) as a metal cleaning and finishing solvent.
(iv) as refrigerant and dewaxing agent.
(v) as a process solvent in the manufacture of drugs.

Harmful Effects (Physiological Effects)

Some of the important harmful effects of methylene chloride are as follows:

(i) It harms the human central nervous system.
(ii) Exposure to low levels of methylene chloride in air can lead to slightly impaired hearing and vision.
(iii) Exposure to high levels of methylene chloride can cause dizziness, nausea, tingling and numbness in the fingers and toes.
(iv) Direct contact with skin causes intense burning and mild redness of the skin.
(v) Direct contact with eyes can burn the cornea.

TRICHLOROMETHANE

(Chloroform, $CHCl_3$)

Chloroform is a colourless, oily liquid with a peculiar sickly smell and a burning taste.

It is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride also called phosgene. It is therefore, stored in dark coloured bottles.

$$2CHCl_3 + O_2 \xrightarrow{\text{Sunlight}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

Preservation of Chloroform

To prevent the oxidation of chloroform, it is preserved in the following ways:

(i) Chloroform is stored in dark coloured bottles to protect it from sunlight to avoid their oxidation.
(ii) These bottles are completely filled with chloroform upto the brim and are properly stoppered to keep air out.
(iii) 1% ethanol is added so, as to convert phosgene gas to diethyl carbonate which is non-volatile and non-toxic.

$$\underset{\text{Phosgene}}{COCl_2} + 2C_2H_5OH \longrightarrow \underset{\text{Diethyl carbonate}}{(C_2H_5)_2CO_3} + 2HCl$$

Uses

It is used

(i) as a solvent for fats, alkaloids, iodine and other substances.
(ii) as a laboratory reagent.
(iii) in the preparation of chloropicrin, chloretone, etc.
(iv) in medicines.
(v) in the production of freon refrigerant, *R*-22.
(vi) as an anaesthetic but now it has been replaced by other anaesthetics such as ether.

Harmful Effects (Physiological Effects)

Some of its harmful effects are:

(i) Chloroform affect the central nervous system. Inhaling it, 900 ppm (in air) for a short time, causes dizziness, fatigue and headache.
(ii) Chronic exposure to chloroform damages liver and kidney due to the formation of phosgene gas inside the body.
(iii) Skin develop sore if immersed directly into the chloroform.

TRIIODOMETHANE
(Iodoform, CHI_3)

It is yellow coloured crystalline solid with characteristic unpleasant odour.

Uses

It is used

(i) as an antiseptic due to the liberation of free iodine.

$$4CHI_3 + 5O_2 \xrightarrow[\text{heat}]{+5O_2} 6I_2 + 4CO_2 + 2H_2O$$

But due to its unpleasant smell, it has been replaced by other formulations containing iodine.

(ii) in the manufacture of pharmaceuticals.

TETRACHLOROMETHANE
(Carbon Tetrachloride, CCl_4)

It is colourless oily liquid with sickly smell. Its boiling point is 350 K. It is formed from chloroform as follows:

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

Uses

It is used

(i) in large quantities, in the manufacture of refrigerants and propellants for aerosol cans.

(ii) as a feed stock in the synthesis of chlorofluoro-carbons (freons) and other chemicals.

(iii) as a cleaning fluid, degreasing agent and spot remover.

(iv) as fire extinguisher.

Harmful Effects (Physiological Effects)

(i) Exposure to CCl_4 causes liver cancer in humans.

(ii) The most common effects are dizziness, light headedness, nausea and vomiting which can cause permanent damage to nerve cells. In severe cases, these effects can lead to coma, unconsciousness or even death.

(iii) Exposure of CCl_4 vapours can make heartbeat irregular or even can stop it. When brought in contact with eyes, it may cause irritation in eyes.

(iv) It is also harmful to environment. When it is released in air, it rises in the atmosphere and depletes the ozone layer. Depletion of ozone layer increases the human exposure to UV rays which lead skin cancer, eye diseases and disorders and possible disruption of the immune system.

FREONS

Chlorofluorocarbon compounds (CFC) of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Freon-12 (dichlorodifluoromethane, CCl_2F_2) is one of the most common freons in industrial use. It is manufactured from tetrachloromethane by **Swarts reaction**.

$$3CCl_4 + 2SbF_3 \xrightarrow{SbCl_5} 2SbCl_3 + \underset{\text{Freon-12}}{3CCl_2F_2}$$

Uses

(i) These are used as refrigerants in refrigerators and air conditioning.

(ii) These are used as propellants for aerosols and foams to spray out deodorants, cleansers, shaving creams, hair sprays and insecticides.

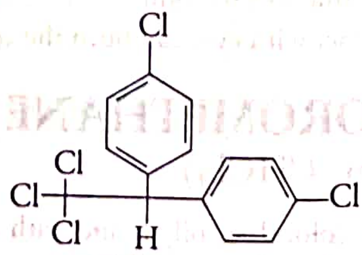
(iii) In stratosphere, freon is able to initiate chain reactions that can result in depletion of ozone layer. Since, freon has been found to be one of the factors responsible for the depletion of ozone layer, they are being replaced by other harmless compounds in many countries.

Harmful Effects (Environmental Effects)

Most freons make its way into the atmosphere, where it undergoes photochemical decomposition and initiates radical chain reactions for depletion of the ozone layer. Therefore, the use of freons as propellants and refrigerants has been drastically discouraged.

p,p'-DICHLORODIPHENYLTRICHLOROETHANE (DDT)

DDT, the first chlorinated organic insecticide, was originally prepared in 1873. **Paul Muller** was awarded the Nobel prize in medicine and physiology in 1948 for this discovery.



(DDT)

It is a white powder, insoluble in water but soluble in oil.

Uses

(i) DDT is a cheap but powerful insecticide.

(ii) It is popularly very effective against anopheles, mosquitoes (causes malaria) and lices which carry typhus.

Harmful Effects (Environmental and Physiological Effects)

DDT is non-biodegradable and extremely stable compound which acts as water pollutant and kills aquatic animals thus imbalancing the water ecosystem. When higher animals (including humans) feed on dead fishes killed by DDT, it enters in their food chains. DDT gets stored in fat tissues of animal and increases in amount over the time. Researches have shown that such deposition in long run may cause cancer and other harmful diseases. Hence, DDT has been banned in many countries but it is still in use, due to its magical effects of controlling disease, in most of the developing countries.

TOPIC PRACTICE 4

OBJECTIVE Type Questions

1. Chloroform can be obtained from
   (a) methanol (b) methanal
   (c) propanol-1 (d) propan-2-ol

2. What of the following is formed? When chloroform reacts with concentrated nitric acid?
   (a) $CHCl_3NO_2$ (b) $C(NO_2)Cl_3$
   (c) CCl_3CNO_2 (d) $CHCl_2NO_2$

3. Chloroform is slowly oxidised by air in the presence of light to form
   (a) phosgene (b) formic acid
   (c) formyl chloride (d) methyl chloride

4. With which mixture carbylamine test is performed in the presence of alc. KOH?
   (a) Chloroform and silver powder
   (b) Tri halogenated methane and one primary amine
   (c) One alkyl halide and one 1° amine
   (d) One alkyl cyanide and one 1° amine

5. Which one does not give iodoform test?
   (a) Ethanol (b) Benzophenone
   (c) Ethanal (d) Acetophenone

6. Choose the incorrect statement among the following :
   (a) In polyhalogen compounds, more than one halogen atom is present
   (b) Dichloromethane is used as paint remover
   (c) Chloroform is used as an anaesthetic in surgery
   (d) Chloroform is also used as paint remover

7. Which of the following effects is/are caused by exposure to CCl_4?
   (a) Liver cancer in human
   (b) Damage to nerve cells
   (c) Coma, unconsciousness
   (d) All of the above

8. When freon is manufactured by tetrachloromethane, the reaction involved in this process is called
   (a) Sandmeyer reaction
   (b) Swarts reaction
   (c) Finkelstein reaction
   (d) All of these

9. Freons, hydrofluorocarbons and fluorocarbons are stable in the stratosphere which are used in
   (a) aerosol propellants
   (b) air conditioning equipments
   (c) refrigeration
   (d) All of the above

10. IUPAC name of DDT is
   (a) 1,1-*bis* (4-chlorophenyl)-2,2,2-trichloroethane
   (b) 1,2-*bis* (4-chlorophenyl)-1,1,1-trichloroethane
   (c) 2,2-*bis* (4-chlorophenyl)-1,1,1-trichloroethane
   (d) 2,1-*bis* (4-chlorophenyl)-1,1,1-trichloroethane

VERY SHORT ANSWER Type Questions

11. Write one use for each of the following.
   (i) DDT (ii) Iodoform **All India 2019**

12. Which polyhalogen compound is used in the production of freon refrigerant *R*-22?

13. Name the non-volatile, non-toxic compound, which is formed when 1% ethanol is added to the bottles of chloroform to convert phosgene gas to that compound.

14. Chloroform is stored in closed dark coloured bottles completely filled, so that air is kept out. Explain. **Delhi 2013, 2010 C**

15. Iodoform has antiseptic properties. Give one reason to support it. **Delhi 2012**

SHORT ANSWER Type I Questions

16. (i) Give the reaction for the formation of phosgene gas.
   (ii) What happens when phosgene gas reacts with ethanol? (Give chemical reaction only).

LONG ANSWER Type Questions

17. Name the following polyhalogen compounds.

(i) Compound that act as a propellant in aerosols.

(ii) Compound that is used in the preparation of chloropicrin.

(iii) Compound that act as fire extinguisher.

(iv) Compound that is a cheap insecticide.

(v) Compound that is used in hair sprays.

18. Some halogen containing compounds are useful in daily life. Some compounds of this class are responsible for the environmental degradation like pollution, exposure of flora and fauna to more and more of UV light etc., which causes destruction to a great extent.

Name the class of these halo compounds. Discuss useful and harmful effects of halogen compounds. In your opinion, what should be done to minimise harmful effects of these compounds?

HINTS AND EXPLANATIONS

1. (*d*) CH_3CO— or $CH_3CH(OH)$— bearing compounds give haloform on reaction with NaOH / X_2. Thus,

$$CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3 + [O] \xrightarrow[-\,2HCl]{Cl_2} CH_3COCH_3$$

$$CH_3COCH_3 + 3Cl_2 + 4NaOH \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Sodium acetate}}{CH_3COONa} + 3NaCl + 3H_2O$$

2. (*b*) $$\underset{}{CHCl_3} + \underset{\text{Conc.}}{HNO_3} \xrightarrow{\text{Heat}} \underset{\substack{\text{Nitrochloroform}\\ \text{(chloropicrin) (Tear gas)}}}{Cl_3CNO_2} + H_2O$$

Chloropicrin is formed when chloroform reacts with concentrated HNO_3.

3. (*a*) $$CHCl_3 + [O] \xrightarrow{\text{Light and air}} CCl_3OH \xrightarrow{\Delta} HCl + \underset{\text{Phosgene}}{Cl_2C{=}O}$$

4. (*b*) $$\underset{1^\circ\text{-amine}}{CH_3NH_2} + \underset{\text{Tri halogenated methane}}{CHI_3} + 3KOH \xrightarrow{\text{Heat}} \underset{\text{Methyl isocyanide}}{CH_3-N{\rightleftarrows}C}$$

5. (*b*) Those compound which have $CH_3-\overset{\overset{\displaystyle O}{||}}{C}-$ or $CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-$ groups give iodoform test. Thus, benzophenone ($C_6H_5COC_6H_5$) will not give iodoform test.

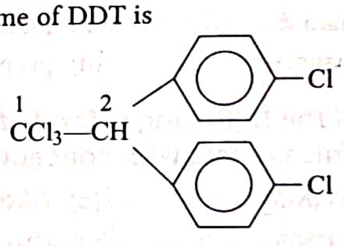
6. (*d*) Chloroform is not used as paint removers.

7. (*d*) Exposure to carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting which cause permanent damage to nerve cells. In severe cases, these effects can lead rapidly to coma, unconsciousness or death.

8. (*b*) Manufacturing of freon from tetrachloromethane is referred as Swarts reaction.

9. (*d*) Freons, hydrofluorocarbons and fluorocarbons are used in aerosol propellants, air conditioning equipments and for refrigeration. These compounds are stable in the stratosphere.

10. (*c*) IUPAC name of DDT is



2, 2-bis (4-chlorophenyl)-1, 1, 1-trichloroethane

11. (i) As an antiseptic

(ii) Powerful insecticide

12. Chloroform ($CHCl_3$)

13. Diethyl carbonate

14. In the presence of light, chloroform is oxidised by air to form an extremely poisonous gas, phosgene (carbonyl chloride). It is therefore, stored in dark coloured completely filled bottles, so that air is kept out.

$$2CHCl_3 + O_2 \xrightarrow{h\nu} 2\underset{\text{Phosgene}}{O{=}C\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix}} + 2\,HCl$$

15. The antiseptic properties of iodoform is due to free I_2, which is liberated when iodoform comes in contact with skin.

$$4CHI_3 + 5O_2 \xrightarrow[\text{Air, heat}]{\text{Moisture}} 6I_2 + 4CO_2 + 2H_2O$$

16. (i) $$2CHCl_3 + O_2 \xrightarrow[\text{Light}]{\text{Air or}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

(ii) $$\underset{\text{Phosgene}}{COCl_2} + \underset{\text{Ethanol}}{2C_2H_5OH} \longrightarrow \underset{\text{Diethyl carbonate}}{(C_2H_5)_2CO_3} + 2HCl$$

17. (i) Carbon tetrachloride (CCl_4)
(ii) Chloroform ($CHCl_3$)
(iii) Carbon tetrachloride (CCl_4)
(iv) DDT
(v) Freons

18. The mentioned halo compounds belong to the class of polyhalogen compounds.

Dichloromethane It is used as a solvent, as a paint remover, as a propellant in aerosols and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent.

Trichloromethane It is employed as a solvent for fats, alkaloids, iodine and other substances.

Triiodomethane It is used as an antiseptic. Now, it has been replaced by some other compounds, because of its objectionable smell.

But some compounds of this class are responsible for exposure of flora and fauna to more and more of UV light which causes destruction to great extent.

These are as follows :

(i) **Tetrachloromethane** When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer. Depletion of the ozone layer is believed to increase human exposure to UV rays leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system. These UV rays cause damage to plants, and reduction of plankton populations in the ocean's photic zone.

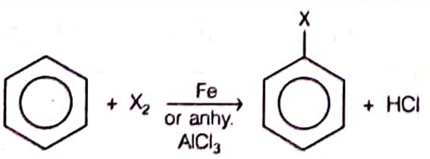
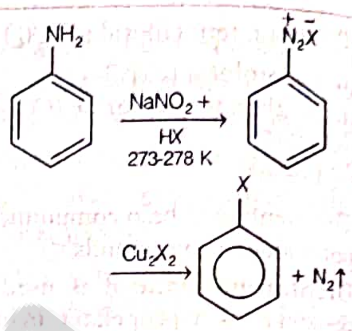
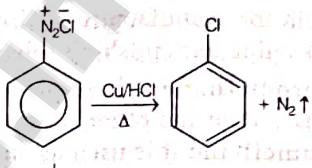
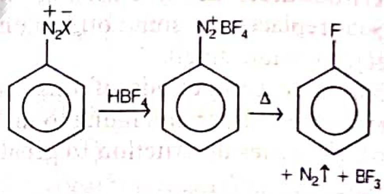
(ii) **Freons** Freon-113 is likely to remain in the air long enough to reach the upper atmosphere. Here, it provides chlorine atoms which damage the ozone layer. Because of this depletion, UV rays enters in our atmosphere and become responsible for the damage to great extent.

(iii) *p*-*p*′-**dichlorodiphenyltrichloroethane** (DDT) It is non-biodegradable. It gets deposited in fatty tissues. If ingestion continues for a long time, DDT builds up within the animal and affect the reproductive system.

To minimise the harmful impacts of these compounds (i.e. freons, hydrofluorocarbons), fluorocarbons and hydrocarbons can be straight used to make refrigerants and air-conditioning equipments. They are stable in the stratosphere and are safe for flora and fauna.

SUMMARY

- Organic compounds formed by the replacement of one or more hydrogen atoms of aliphatic hydrocarbon, by an equal number of halogen atoms are called haloalkanes. Haloarenes are compounds having halogen atom directly attached to the aromatic ring.
- In IUPAC system, these are written by prefixing the word 'halo' to the name of the longest straight chain alkane.
- Haloarenes are the common as well as IUPAC names of aryl halides. For dihalogen derivatives, the prefixes, *o* -, *m* - and *p* - are used in common system but in IUPAC system the numerals 1, 2; 1, 3 and 1, 4 are used.
- **Preparation**

Method	Reaction involved
(i) From alcohols (substitution)	$RCH_2OH + HX \longrightarrow RCH_2X + H_2O$, $R—OH \xrightarrow[(P_4/X_2)]{PX_3} R—X + H_3PO_3$, $R—OH + SOCl_2 \xrightarrow{\Delta} R—Cl + SO_2\uparrow + HCl\uparrow$
(ii) From alkanes (halogenation)	$CH_4 \xrightarrow{Cl_2/h\nu} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$
(iii) From alkenes (addition) • Addition of hydrogen halides	$R—CH{=}CH—R + HX \longrightarrow R—CH_2—CH(X)—R'$
• Addition of halogen	$H_2C{=}CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2—CH_2Br$
• Allylic substitution of alkenes	$CH_3CH_2CH{=}CH_2 + X_2 \xrightarrow[\text{or NBS}]{773\text{ K}} CH_3\underset{\displaystyle X}{CH}—CH{=}CH_2 + HX$
(iv) By halide exchange reaction	$H_3C—Br + AgF \xrightarrow[\text{acetone}]{\text{Dry}} H_3C—F + AgBr$ (Swarts reaction)
(v) Halogenation	
(vi) From benzene diazonium salts Sandmeyer's reaction	
Gattermann reaction	
Balz-Schiemann reaction	

- **Physical properties**
  - **Haloalkanes** Polar in nature, insoluble in polar solvents like water as they do not have the ability to form hydrogen bond with water, density increases with increase in the number of alkyl groups.
  - **Haloarenes** They are solids, less polar compounds, insoluble in water but soluble in organic solvents like ethanol and ether.
  - Boiling point increases as the size of halogen atom increases and also as the size of aryl group increases.
  - When alkyl group is same, melting point increases as size of halogen increases. For dihalobenzenes, *p*-isomer has high melting point as its molecules pack closely in the crystal lattice.
  - The dipole moments of haloarenes increases in the order; fluorobenzene < chlorobenzene < bromobenzene < iodobenzene.
- Alkyl halides, give nucleophilic substitution, elimination reaction, reduction reaction with metals and Friedel-Craft's alkylation.
- **Polyhalogen compounds**
  - **Dichloromethane** It is colourless, sweet smelling, volatile liquid, having low boiling point of 313 K and specific gravity of 1.37. It is used as solvent, paint remover, propellant, refrigerant and dewaxing agent.
  - **Chloroform** $CHCl_3$ is slowly oxidised by air in the presence of light to an extremely poisonous gas carbonyl chloride, also known as phosgene.
  - **Iodoform** CHI_3 is yellow coloured crystalline solid with characteristic unpleasant odour.
  - **Tetrachloromethane** CCl_4 is a colourless, oily liquid with sickly smell.
  - **Freons** CFC of methane and ethane are collectively known as freons.

CHAPTER PRACTICE

OBJECTIVE Type Questions

1 The IUPAC name of isobutyl bromide is **CBSE 2021 (Term I)**

(a) 1-bromo-3-methylbutane
(b) 3-bromo-2-methylpropane
(c) 2-bromo-2-methylpropane
(d) 1-bromo-2-methylpropane

2 Chlorobenzene when treated with sodium in dry ether gives diphenyl. It is called **CBSE 2021 (Term I)**

(a) Wurtz reaction
(b) Fittig reaction
(c) Wurtz-Fittig reaction
(d) Friedel-Crafts reaction

3 Which reagent is required for one step conversion of benzene diazonium chloride to bromobenzene? **CBSE 2021 (Term I)**

(a) PBr_3 (b) HBr (c) Cu_2Br_2 (d) Br_2

4 Which of the following compounds undergoes racemisation on hydrolysis with aqueous KOH? **CBSE 2021 (Term I)**

(a) $CH_3—CH_2—Br$
(b) $CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}H}—CH_2—Br$
(c) $CH_3—Br$
(d) $CH_3—\overset{\displaystyle C_2H_5}{\overset{|}{C}H}—Br$

5 Aryl halide are extremely less reactive towards nucleophilic substitution reaction due to

(a) resonance effect
(b) unstability of phenyl cation
(c) repulsion between π-cloud of benzene ring and incoming nucleophile
(d) All of the above

CASE BASED Questions

Case I

Nucleophilic substitution reaction of haloalkane can be conducted according to both S_N1 and S_N2 mechanisms. However, which mechanism it is based on is related to such factors as the structure of haloalkane, and properties of leaving group, nucleophilic reagent and solvent.

Influences of halogen No matter which mechanism the nucleophilic substitution reaction is based on, the leaving group always leave the central carbon atom with electron pair. This is just the opposite of the situation that nucleophilic reagent attacks the central carbon atom with electron pair.

Therefore, the weaker the alkalinity of leaving group is , the more stable the anion formed is and it will be more easier for the leaving group to leave the central carbon atom; that is to say, the reactant is more easier to be substituted. The alkalinity order of halogen ion is $I^- < Br^- < Cl^- < F^-$ and the order of their leaving tendency should be $I^- > Br^- > Cl^- > F^-$.

Therefore, in four halides with the same alkyl and different halogens, the order of substitution reaction rate is $RI > RBr > RCl > RF$. In addition, if the leaving group is very easy to leave, many carbocation intermediates are generated in the reaction and the reaction is based on S_N1 mechanism. If the leaving group is not easy to leave, the reaction is based on S_N2 mechanism.

Influences of solvent polarity In S_N1 reaction, the polarity of the system increases from the reactant to the transition state, because polar solvent has a greater stabilising effect on the transition state than the reactant, thereby reduce activation energy and accelerate the reaction. In S_N2 eaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs.

At this time, polar solvent has a great stabilising effect on Nu than the transition state, thereby increasing activation energy and slow down the reaction rate. For example, the decomposition rate (S_N1) of tertiary chlorobutane in 25°C water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (S_N2) of 2-bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol.

In a word, the level of solvent polarity has influence on both S_N1 and S_N2 reactions, but with different results. Generally speaking, weak polar solvent is favorable for S_N2 reaction, while strong polar solvent is favorable for S_N1 reaction, because only under the action of polar solvent can halogenated hydrocarbon dissociate into carbocation and halogen ion and solvents with a strong polarity is favorable for solvation of carbocation, increasing its stability.

Generally speaking, the substitution reaction of tertiary haloalkane is based on S_N1 mechanism in solvents with a strong polarity (for example, ethanol containing water).

CBSE Question Bank

The following questions are multiple choice questions. Choose the most appropriate answer :

6. S_N1 mechanism is favoured in which of the following solvents

(a) benzene (b) carbon tetrachloride
(c) acetic acid (d) carbon disulphide

7. Nucleophilic substitution will be fastest in the case of

(a) 1-chloro-2,2-dimethyl propane
(b) 1-iodo-2,2-dimethyl propane
(c) 1-bromo-2,2-dimethyl propane
(d) 1-fluoro-2,2-dimethyl propane

8. S_N1 reaction will be fastest in which of the following solvents?

(a) Acetone (dielectric constant 21)
(b) Ethanol (dielectric constant 24)
(c) Methanol (dielectric constant 32)
(d) Chloroform (dielectric constant 5)

9. Polar solvents make the reaction faster as they

(a) destabilise transition state and decrease the activation energy
(b) destabilise transition state and increase the activation energy
(c) stabilise transition state and increase the activation energy
(d) stabilise transition state and decrease the activation energy

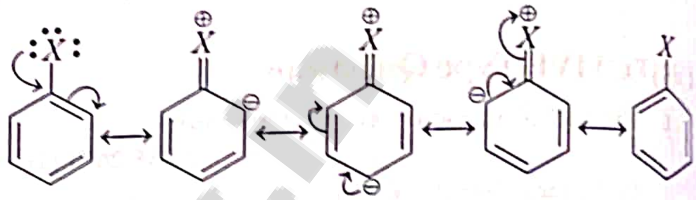
10. S_N1 reaction will be fastest in the case of:

(a) 1-chloro-2-methyl propane
(b) 1-iodo-2-methyl propane
(c) 1-chlorobutane
(d) 1-iodobutane

Case II

Nucleophilic substitution reactions in aryl halides occur only under drastic conditions, whereas electrophilic substitution reactions such as halogenation, nitration, sulphonation and Friedel-Craft's reaction occur easily. In these reactions, stronger electrophile replaces weaker electrophile.

The electrophilic substitution reactions in haloarenes occur slowly and requires more drastic conditions. This is due to the *ortho*- and *para*-directing influence of halogen atom attached to a benzene ring which can be understood by following resonating structures.



In the question that follow Assertion and Reason are given. Reason is purported to the explaination for Assertion. Study carefully and then mark your answers, according to the codes given below.

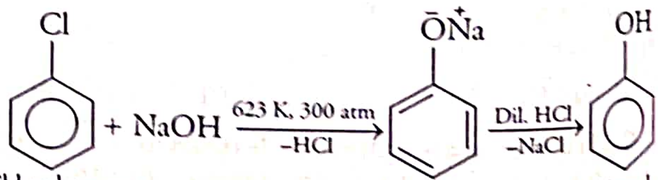
Marks your answer as :

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

11 Assertion Haloarenes are less reactive towards substitution reactions.

Reason The electron pairs on the halogen atom are in conjugation with π-electrons of the ring.

12 Assertion

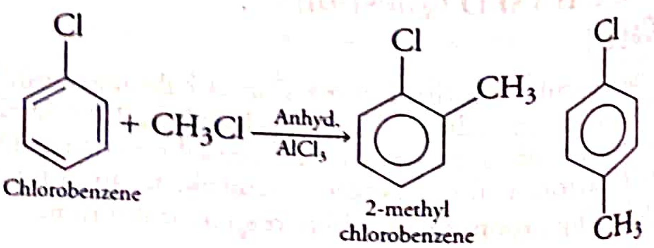


Chlorobenzene (Haloarene) Phenol

Reason It is equation for nucleophilic substitution reaction of haloarene.

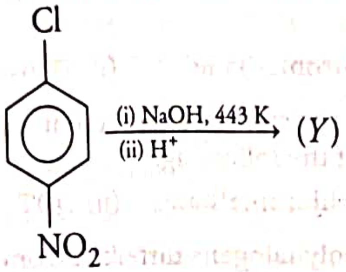
Or **Assertion** Two products formed from Friedel-Craft's alkylation in chlorobenzene.

Reason



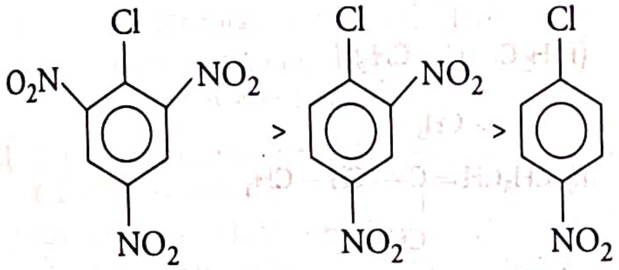
Chlorobenzene 2-methyl chlorobenzene 4-methyl chlorobenzene

13 **Assertion**



Reason Y is 2-nitrophenol.

14 **Assertion**



Reason The order of reactivity towards electrophilic addition reaction.

ASSERTION and REASON

■ Directions (Q. Nos.15-21) *In the following questions. an Assertion (A) is followed by a corresponding Reason (R) Use the following keys to choose the appropriate answer.*

(a) Both (A) and (R) are correct, (R) is the correct explanation of (A).

(b) Both (A) and (R) are correct, (R) is not the correct explanation of (A).

(c) (A) is correct; (R) is incorrect.

(d) (A) is incorrect; (R) is correct.

15 **Assertion** (A) S_N1 reaction is accompanied by racemisation.
Reason (R) Carbocation is formed in this reaction and attack of nucleophile can be from either side of the leaving group.

16 **Assertion** (A) Alkyl halides are insoluble in water. **CBSE 2021 (Term I)**

Reason (R) Alkyl halides have halogen attached to sp^3 hybridised carbon.

17 **Assertion** (A) Bond cleavage in haloarene is difficult than haloalkane.

Reason (R) Phenyl carbocation is more stable.

18 **Assertion** (A) Nitration of chlorobenzene leads to the formation of ortho and para nitrochloro benzene.

Reason (R) $—NO_2$ group is a *o*, *p*-directing group.

19 **Assertion** (A) *neo* pentyl chloride is formed when *neo* pentyl alcohol reacts with HCl.

Reason (R) *neo* pentyl alcohol is a primary alcohol.

20 **Assertion** (A) S_N1 mechanism is ruled out in case of haloarene.

Reason (R) Phenyl cation is formed as a result of self ionisation which is not stabilised by resonance.

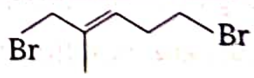
21 **Assertion** (A) Phosphorus chlorides (In and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.
Reason (R) Thionyl chloride give pure alkyl halides.

VERY SHORT ANSWER Type Questions

22 Among the following, which is not an allylic halide?
3-bromo-2-methylpropene, 4-bromobut-1-ene and 3-bromo-2-methylbut-1-ene.

23 Among the following, which nomenclature is not according to the IUPAC system?
1-bromoprop-2-ene, 2-methyl-3 phenylpentane and 5-oxohexanoic acid.

24 Write the IUPAC name of the following compound



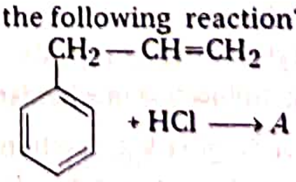
25 Write the IUPAC name of the compound $(CH_3)_3CCH_2Br$.

26 Write the structure of the compound 1-chloro-4-ethylcyclohexane.

27 Write the structure of the following compound, 2-chloro-3-methylpentane
NCERT Intext; NCERT; All India 2011C

28 Write the structure of 1-bromo-4-chlorobut-2-ene.
Delhi 2017

29 What is A in the following reaction?



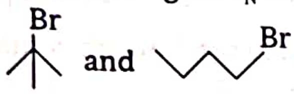
30 How can the following conversion be carried out?
Aniline to bromobenzene. **All India 2015**

31 Arrange the following compounds in the order of increasing boiling points. Chloromethane, chloroform, iodomethane, bromomethane.

32 Write a chemical reaction in which iodide ion displaces diazonium group from diazonium salt.

33 Why iodoform has appreciable antiseptic property?

34 In the following pairs of halogen compounds, which compound undergoes S_N2 reaction faster?



35 An alcohol having molecular formula, $C_4H_{10}O$ is optically active. What is its structure?

36 What happens when CH_3—Br is treated with KCN?
Delhi 2013

37. A solution of KOH hydrolyses $CH_3CHClCH_2CH_3$ and $CH_3CH_2CH_2CH_2Cl$. Which one of these is more easily hydrolysed?

38 What is the IUPAC name of DDT? Why is its use banned in many countries?

SHORT ANSWER Type I Questions

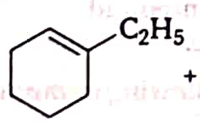
39 Account for the following :
(i) *p*-dibromobenzene has higher melting point than *o*-dibromobenzene.
(ii) *n*-butyl bromide reacts faster than *t*-butyl bromide through S_N2 mechanism.

40 Why is iodination of benzene difficult?

41 Write the mechanism of the following reaction.

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

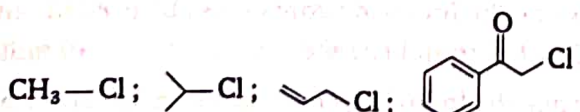
42 Complete the following reactions.

(i)  + HI ⟶

(ii) $CH_3CH_2CH=CH_2 + HBr \longrightarrow$

43 Suggest a possible reason for the following observations:
(i) The order of reactivity of haloalkanes is $RI > RBr > RCl$.
(ii) *Neo*-pentyl chloride, $(CH_3)_3C—CH_2Cl$ does not follow S_N2 mechanism.

44 *P*, *Q*, *R* and *S* undergoes S_N2 reaction with KI in acetone. What is the order of the rate of reaction?



P *Q* *R* *S*

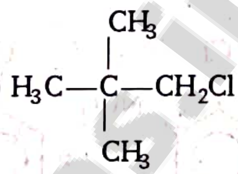
45 Why are haloarenes more stable than haloalkanes and undergo electrophilic substitution reaction at *o*- and *p*-position?

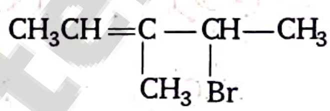
46 Write the reaction for the formation of each of the following.
(i) Dichloromethane (ii) Phosgene

47 Write one physiological and environmental effect for each of the following.
(i) Tetrachloromethane (ii) DDT **Delhi 2019**

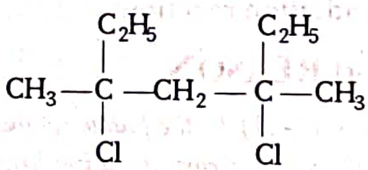
48 How are polyhalogens different from other organic halogens? Explain with example.

49 Give the IUPAC names of the following compounds.

(i) 

(ii) 

(iii) $(CH_3)_3CCH_2—CH_2Cl$

(iv) 

All India 2010 C

50 Why is sulphuric acid not used during the reaction of alcohols with KI? **NCERT Intext**

51 (i) Allyl chloride is hydrolysed more readily than *n*-propylchloride. Why?
(ii) Cyanide ion acts as an ambident nucleophile. From which end, it acts as a stronger nucleophile in aqueous medium and why?

52 Out of $C_6H_5CHClC_6H_5$ and $C_6H_5CH_2Cl$, which is more easily hydrolysed by aqueous KOH? **NCERT**

53 Diphenyls are potential threat to the environment. How are these produced from aryl halides?
NCERT Exemplar

SHORT ANSWER Type II Questions

54 Classify the haloalkanes on the basis of hybridisation of their $C-X$ bonds alongwith examples.

55 Write the IUPAC name, structure and one isomer for each of the following compounds.
(i) *tert*-butyl bromide (ii) Allyl chloride

56 Which one of the following pair undergo S_N1 reaction faster and why?
$H_2C=CHCHClCH_3$ or $CH_3-CH_2CHClCH_3$

57 How will you obtain monobromobenzene from aniline? Give reaction.

58 Give reasons for the following observations.
(i) p-dibromobenzene has higher melting point than those of o- and m-isomers.
(ii) Out of chlorobenzene and chloromethane, which is more reactive towards nucleophilic substitution reaction?
(iii) Racemisation occurs in S_N1 reaction.

59 How would you differentiate between S_N1 and S_N2 mechanisms of the substitution reactions? Give one example of each.

60 How will you bring about the following conversions?
(i) 1-bromobutane to 2-bromobutane
(ii) Aniline to chlorobenzene
(iii) Ethanol to ethyl bromide

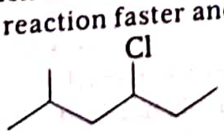
61 Explain the formation of the two products in the following reaction:
$CH_3\,CH{=}CHCH_2\,Cl + H_2\,O \longrightarrow$
$CH_3\,CH{=}CHCH_2\,OH + CH_3\,CH(OH)CH{=}CH_2$

62 (i) Why is ether preferred over chloroform as anaesthetic agent?
(ii) Name the polyhalogen which is used to prepare chloropicrin?

63 Classify the following compounds as primary, secondary and tertiary halides.
(i) 1-bromobut-2-ene
(ii) 4-bromopent-2-ene
(iii) 2-bromo-2-methylpropane **NCERT Exemplar**

64 Write the equations for the preparation of 1-iodobutane from
(i) 1-butanol (ii) 1-chlorobutane
(iii) but-1-ene **NCERT**

65 (i) Comment on the strength and size of the nucleophile or base.
Or Chlorobenzene is extremely less reactive towards a nucleophilic substitution reaction. Give two reasons for the same. **Delhi 2013**
Or Why aryl halides are less reactive towards nucleophilic substitution reactions than alkyl halides?
(ii) Which of the following two substances undergo S_N1 reaction faster and why? **NCERT Exemplar**



Or


66 Arrange the compounds of each set in the order of reactivity towards S_N2 displacement.
NCERT; All India 2011
(i) 2-bromo-2-methylbutane, 1-bromopentane, 2-bromopentane
(ii) 1-bromo-3-methylbutane, 2-bromo-2-methyl butane, 2-bromo-3-methylbutane
(iii) 1-bromobutane, 1-bromo-2, 2-dimethylpropane, 1-bromo-2-methylbutane, 1-bromo-3-methyl butane

67 What will be the major organic product of the following reactions?
(i) 

$\xrightarrow{SOCl_2}$

(ii) $CH_3{-}C(CH_3)_2{-}Br \xrightarrow[\text{Ethanol, heat}]{KOH}$

(iii) $CH_3CH{=}C(CH_3)_2 \xrightarrow[\text{Peroxide}]{HBr}$

LONG ANSWER Type Questions

68 (i) What are enantiomers? Draw the structures of the possible enantiomers of Butan-2-ol.
(ii) Optically active 2-bromobutane, on treatment with NaI in acetone gives a product, which does not show optical activity. Give reason.
(iii) An optically active compound with molecular formula of C_7H_{15} Br, reacts with aqueous KOHt o give a racemic mixture of products. Write the mechanism involved for this reaction.

69 The following reaction gives two products:
$C_6H_5CH_2CHClC_6H_5 \xrightarrow[\text{heat}]{\text{Alc.KOH}}$
Explain the formation of the products and write their structures.

70 (i) Account for the following :
(a) Use of DDT was banned in United States in 1973.
(b) Alkyl halides prefer to undergo dehydrohalogenation in the presence of a strong base such as Na metal, instead of undergoing Wurtz reaction.
(c) Allyl chloride is more reactive than the n-propyl chloride towards nucleophilic substitution reaction. Explain why?
(ii) What happens, when
(a) ethyl chloride is treated with aqueous KCN?
(b) chlorobenzene is subjected to replace of hydroxyl group.

ANSWERS

1 (d) **2** (b) **3** (c) **4** (d) **5** (d)

6 (c) A polar protic solvent i.e. acetic acid favour S_N1 mechanism. Higher the polarity of the solvent, stronger's the solvent interaction and thus faster is the ionisation of *RX* and consequently faster is the S_N1 reaction.

7 (*b*) Weaker the alkalinity of leaving group, more stable is the anion formed. It will be more easier for leaving groups to leave the central carbon atom.

The relative reactivity order of substitution reaction,

$$RI > RBr > RCl > RF$$

So, 1-iodo-2, 2-dimethyl propane will give fastest nucleophilic substitution reaction.

8 (c) Solvent which have highest dielectric constant, will give fastest S_N1 reaction. In the given solvents methanol has highest dielectric constant, so it will give fastest S_N1 reaction.

9 (*d*) Polar solvent have large dipole moments. They are lower in energy of both reactant and transition state. Due to lower activation energy, reaction goes faster.

10 (*b*) The order of substitution reaction rate is

$$RI > RBr > RCl > RF$$

Reaction will be fastest in case of 1-iodo-2-methyl propane. In 1-iodo-2-methyl propane, 1° carbocation formed in the reaction rearranges itself to 2° carbocation.

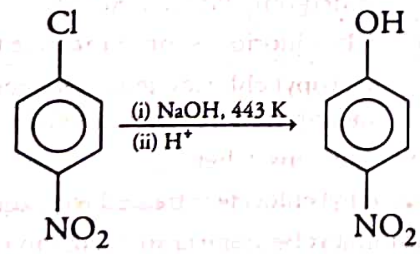
11 (*a*) This is because, in haloarenes, the electron pairs on the halogen atom are in conjugation with π-electrons of the ring. As a result, the C—Cl bond acquires partial double bond character. Therefore, the bond cleavage in halogens is difficult than haloalkanes in which carbon is attached to halogen by a pure single bond. Hence, haloarenes are less reactive than haloalkanes.

Both (A) and (R) true and (R) is the correct explanation of (A).

12 (*b*) Both (A) and (R) are true but (R) is not correct explanation of (A).

Or (*a*) Both (A) and (R) are true. (R) is correct explanation of (A).

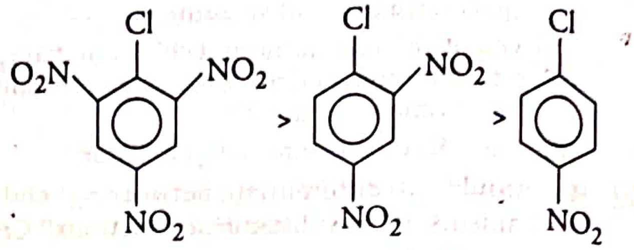
13 (*c*) *Y* is 4-nitrophenol. The reaction is as follows



4-chloronitrobenzene 4-nitrophenol (*Y*)

Only (A) is correct.

14 (*c*) The correct order of reactivity towards nucleophilic substitution reaction of the given compounds is as follows :



Only (A) is correct.

15 (*a*) In case of optically active alkyl halides, S_N1 reactions are accompanied by racemisation. The carbocation formed in the slow step being sp^2-hybridised is planar (achiral). The attack of the nucleophile may be from either side resulting mixture of products. One product has same configuration, while other has opposite configuration. Thus, both (A) and (R) are correct and (R) is the correct explanation of (A).

16 (b) Here, both (A) and (R) are true but (R) is not the correct explanation of (A).

Alkyl halides are insoluble in water because they are unable to form hydrogen bonds with water or break pre-existing hydrogen bonds.

17 (c) (A) is correct but (R) is incorrect. Bond cleavage in haloarene is difficult than haloalkane due to partial double bond character in C—Cl bond because of resonance, so it is less reactive towards nucleophilic substitution reaction. Phenyl carbocation is very unstable.

18 (c) (A) is correct but (R) is incorrect. Presence of —Cl in chlorobenzene activates the ring at *ortho* and *para*-positions and therefore, nitration of chlorobenzene leads to the formation of *o*- and *p*-chloro nitro chlorobenzene. $—NO_2$ group is a *meta*-directing group.

19 (*d*) 2- chloro -2 methylbutane (not neo pentyl chloride) is formed when neo pentyl alcohol reacts with HCl. The initially formed primary carbocation undergoes rearrangement to form more stable tertiary carbocation. The reaction is given as follows :

$$\underset{\text{(Primary alcohol)}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2OH} \xrightarrow[-H_2O]{HCl} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2CH_3$$

Therefore, (A) is incorrect but (R) is correct statement.

20 (*a*) In case of haloarenes, the phenyl cation formed as a result of self ionisation will not be stabilised by resonance and therefore S_N1 mechanism is ruled out. Thus, both (A) and (R) are correct and (R) is correct explanation of (A).

21 (*b*) (A) is not correct but (R) is correct. In fact, the use of thionylchloride is preferred over phosphorus chlorides for preparing haloalkanes from alcohols because the

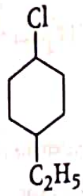
other products of the reaction (i.e.) HCl(g) and $SO_2(g)$ being gases escape out leaving behind pure haloalkane.

22 4-bromobut-1-ene **23** 1-bromoprop-2-ene

24 1, 5- dibromo-2-methylpent-2-ene

25 1- bromo-2,2-dimethylpropane

26



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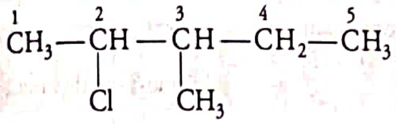

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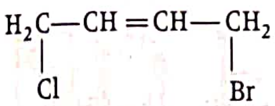
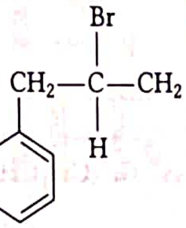


29 A =



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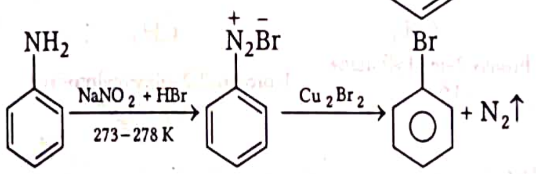
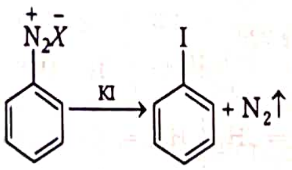


31 Chloroform>Iodomethane>Bromomethane>Chloromethane

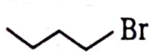
32 Replacement of the diazonium group by iodine is done simply by shaking the diazonium salt with potassium iodide.



33 Iodoform has appreciable antiseptic properties due to the liberation of free iodine.

$$HCHI_3 + 5O_2 \xrightarrow[\text{heat}]{SO_2} 6I_2 + 4CO_2 + 2H_2O$$

34



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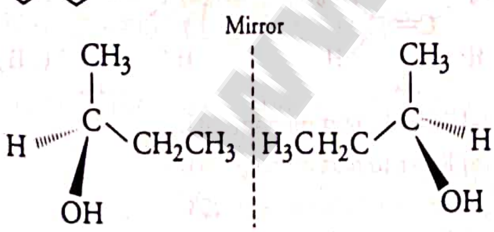


36 When CH_3Br is treated with KCN then methyl cyanide (CH_3CN) is formed.

$$CH_3Br + KCN \longrightarrow CH_3CN + KBr$$

37 $CH_3CHClCH_2CH_3$ upon ionisation gives more stable 2° carbocation while $CH_3CH_2CH_2CH_2Cl$ gives less stable 1° carbocation.

38 The IUPAC name of DDT is 2, 2-*bis*-(4-chlorophenyl)-1, 1, 1-trichloroethane. It is non-biodegradable and extremely stable compound which act as a water pollutant and kills aquatic animals thus inbalancing the water ecosystem.

39 (i) Refer to solution 12 on page 240.
(ii) Refer to text on pages 226 and 227.

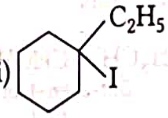
40 Refer to text on page 217.

41

$$C_2H_5-\ddot{O}H + H^+ \longrightarrow C_2H_5-\overset{+}{\ddot{O}}H_2$$

$$\bar{X} + R-\overset{+}{O}H_2 \longrightarrow C_2H_5-X + H_2O$$

42 (i)



(ii) $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

43 (i) Refer to text on page 228 (ii) Refer to text on page 227 and 228.

44 Refer to text on pages 227 and 228.

45 Refer to text on pages 223 and 224.

46 (i) $CH_4 + 2Cl_2 \xrightarrow{hv} CH_2Cl_2 + 2HCl$

(ii) $2CHCl_3 + O_2 \xrightarrow{hv} 2COCl_2 + 2HCl$

47 (i) Refer to text on page 248. (ii) Refer to text on page 249.

48 Refer to text on page 247.

49 (i) 1-chloro-2, 2-dimethylpropane
(ii) 4-bromo-3-methylpent-2-ene
(iii) 1-chloro-3, 3-dimethylbutane
(iv) 3, 5-dichloro-3, 5-dimethylheptane

50 Refer to text on page 215.

51 (i) Refer to text on page 227 and 228.
(ii) Refer to text page 225.

52 In S_N1 reaction, $C_6H_5CHClC_6H_5$ gets hydrolysed more easily than $C_6H_5CH_2Cl$.
However, under S_N2 reaction, $C_6H_5CH_2Cl$ (with lesser steric hindrance) gets hydrolysed more easily than $C_6H_5CHClC_6H_5$. Refer to text on pages 227 and 228.

53 In environment, diphenyl is formed during the incomplete combustion of mineral oil and coal. It is present in the exhaust gases of vehicles and in exhaust air from residential and industrial heating devices.Acute exposure to high levels of diphenyl has been observed to cause eye and skin irritation and toxic effect on the liver, kidneys and central/peripheral nervous system. Kidneys of animals are also affected due to the ingestion of biphenyls.]

Fittig reaction (Preparation of diphenyls from aryl halides). Refer to text on page 235.

54 Refer to text on pages 207 and 208.

55 (i) Refer to text on page 208.
(ii) Allyl chloride ($CH_2 = CH - CH_2Cl$)
Isomer of $CH_2 = CH-CH_2Cl$ (allyl chloride) is
$CH_3- CH = CH-Cl$ (1-chloroprop-1-ene)

56 $CH_2 = CHCHClCH_3$, due to the delocalisation.

57 Refer to text on page 217.

58 (i) Refer to text on page 224.
(ii) Refer to text on pages 227 and 233.
(iii) Refer to text on pages 230.

59 Refer to text on pages 226, 227 and 228.

60 (i) Dehydrohalogenation followed by Markovnikov's addition.
(ii) Refer to text on page 217.
(iii) Refer to text on page 215.

61 1-chloro but-2-ene undergoes hydrolysis in warm water to give a mixture of these allylic alcohols.

$$CH_3CH=CHCH_2Cl \xrightarrow{H_2O} \underset{\text{But-2-en-1-ol}}{CH_3CH=CHCH_2OH} + \underset{\text{But-3-en-1-ol}}{CH_3\overset{OH}{\overset{|}{C}H}CH=CH_2}$$

The two products can be explained by an S_N1 mechanism that produces an allylic cation that can react with water at either 1 or 3 position

$$CH_3CH=CH-\underset{Cl}{\underset{|}{C}H_2} \xrightarrow{S_N1} CH_3CH=CH-\overset{+}{C}H_2 \longleftrightarrow CH_3\overset{+}{C}H-CH=CH_2$$

$$CH_3CH=CH-\overset{+}{C}H_2 \xrightarrow{H_2O} CH_3CH=CHCH_2OH$$

$$CH_3\overset{+}{C}H-CH=CH_2 \xrightarrow{H_2O} CH_3\underset{OH}{\underset{|}{C}H}CH=CH_2$$

62 (i) Refer to text on page 247. (ii) Chloroform ($CHCl_3$)

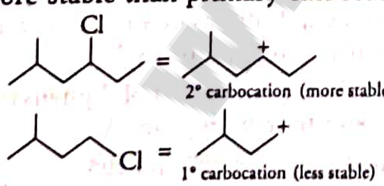
63 (i) Primary halide (ii) Secondary halide
(iii) Tertiary halide

64 (i) $\underset{\text{1-butanol}}{CH_3CH_2CH_2CH_2OH} + HI \xrightarrow{ZnCl_2} \underset{\text{1-iodobutane}}{CH_3CH_2CH_2CH_2I}$

(ii) $\underset{\text{1-chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + NaI \xrightarrow{\text{Dry acetone}} \underset{\text{1-iodobutane}}{CH_3CH_2CH_2CH_2I} + NaCl$

(iii) $\underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} + HBr \xrightarrow{\text{Peroxide}}$
$\underset{\text{1-bromobutane}}{CH_3CH_2CH_2CH_2Br} \xrightarrow[\text{Dry acetone}]{NaI} \underset{\text{1-iodobutane}}{CH_3CH_2CH_2CH_2I}$

65 (i) Refer to text on pages 231 and 232.
(ii) In S_N1 reaction, reactivity depends upon the stability of intermediate carbocation. A secondary carbocation is more stable than primary carbocation.

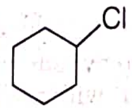


Former carbocation being secondary, is more stable than the latter being primary. Hence, it undergoes S_N1 reaction faster.

66 (i) $\underset{\substack{\text{1-bromopentane}\\(1^\circ)}}{CH_3CH_2CH_2CH_2CH_2Br} > \underset{\substack{\text{2-bromopentane}\\(2^\circ)}}{CH_3\underset{Br}{\underset{|}{C}H}CH_2CH_2CH_3} > \underset{\substack{\text{2-bromo -2-methylbutane (3°)}}}{CH_3\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}CH_2CH_3}$

(ii) $\underset{\substack{\text{1-bromo-3-methyl}\\\text{butane}\\(1^\circ)}}{CH_3\underset{CH_3}{\underset{|}{C}H}CH_2CH_2Br} > \underset{\substack{\text{2-bromo-3-methyl butane}\\(2^\circ)}}{CH_3-\underset{Br}{\underset{|}{C}H}-\underset{CH_3}{\underset{|}{C}H}-CH_3}$
$> \underset{\text{2-bromo-2-methylbutane (3°)}}{CH_3-\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-CH_3}$

(iii) $\underset{\substack{\text{1-bromobutane}\\(1^\circ)}}{CH_3CH_2CH_2CH_2Br} > \underset{\substack{\text{1-bromo-3-methyl butane}\\(1^\circ)}}{CH_3\underset{CH_3}{\underset{|}{C}H}CH_2CH_2Br} >$
$\underset{\substack{\text{1-bromo-2-methylbutane}\\(1^\circ)}}{CH_3CH_2\underset{CH_3}{\underset{|}{C}H}CH_2Br} > \underset{\substack{\text{1-bromo-2,2-dimethylpropane}\\(1^\circ)}}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2Br}$

67 (i) 

$+ SO_2\uparrow + HCl\uparrow$ (ii) $CH_3-\overset{CH_3}{\overset{|}{C}H}=CH_2$

(iii) Refer to text on page 216.

68 (i) Refer to text on page 229.

$$CH_3-CH_2-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\overset{H}{\overset{|}{C}}=CH_2 \quad \vdots \quad H_2C=\overset{H}{\overset{|}{C}}-\overset{H}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2CH_3$$

(ii) Refer to text on page 229 and 230.
(iii) Refer to text on pages 227 and 228.

69

$$\underset{cis}{\overset{H_5C_6}{H}\!\!>C=C<\!\!\overset{C_6H_5}{H}} + \underset{trans}{\overset{H_5C_6}{H}\!\!>C=C<\!\!\overset{H}{C_6H_5}}$$

70 (i) (a) Refer to text on page 247.
(b) Refer to text on page 231.
(c) Refer to text on page 228.
(ii) (a) Refer to solution 226.
(b) Refer to solution 232.

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07

ALCOHOLS, PHENOLS AND ETHERS

Alcohols and phenols are formed by replacing one hydrogen atom from a hydrocarbon (aliphatic or aromatic) by —OH group. They have a variety of applications in industry as well as in day-to-day life. The sugar we eat, the cotton used for fabrics, the paper we use for writing, are all made up of compounds having —OH groups. Similarly, ether plays an important role in pharmacology and medicines, especially for the use of anaesthetics. They are quite volatile. They are also used as solvents and plasticisers.

This chapter includes the chemistry of these three classes of compounds, namely alcohols, phenols and ethers.

CHAPTER CHECKLIST

- Alcohols and Phenols
- Ethers

|TOPIC 1|

Alcohols and Phenols

An alcohol contains one or more hydroxyl group(s) (—OH), directly attached to carbon atom(s) of an aliphatic system (like CH_3OH) while a phenol contains —OH group(s), directly attached to carbon atom(s) of an aromatic system (like C_6H_5OH).

CLASSIFICATION

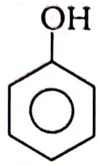
These may be classified as mono-, di-, tri- or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups respectively, in their structures.

(i) **Monohydric** Alcohols having one hydroxyl group (—OH) attached to the carbon atom of a compound, are monohydric.

e.g.

CH_3OH , CH_3CH_2OH ,

Methanol Ethanol



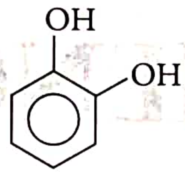
Phenol

(ii) **Dihydric** Alcohols having two hydroxyl groups (—OH) attached to the two carbon atoms of a compound, are dihydric.

e.g.

CH_2—OH
|
CH_2 ,
|
CH_2—OH

Propane-1,3-diol



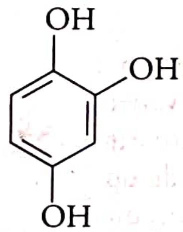
Catechol

(iii) **Trihydric** Alcohols having three hydroxyl groups (—OH) attached to the three carbon atoms of a compound, are trihydric.

e.g.

CH_2OH
|
CHOH ,
|
CH_2OH

Glycerol



Hydroxyquinol

Classification of Monohydric Alcohols

Monohydric alcohols may be further classified according to the hybridisation of the carbon atom to which the hydroxyl group is attached.

Compounds containing C_{sp^3}—OH Bond

In this class of alcohols, the —OH group is attached to a sp^3 hybridised carbon atom of an alkyl group.

They are further classified as follows:

Primary, Secondary and Tertiary Alcohols

In these alcohols, the —OH group is attached to primary, secondary and tertiary carbon atom respectively.

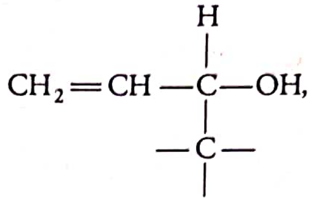
e.g. —CH_2OH, Primary (1°) ; >CHOH, Secondary (2°) ; $\geq$COH, Tertiary (3°)

Allylic Alcohols

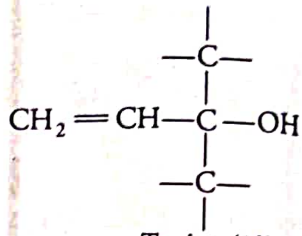
In these alcohols, the —OH group is attached to a sp^3 hybridised allylic carbon (i.e. carbon atom next to the carbon-carbon double bond).

e.g. $CH_2=CH—CH_2—OH$,

Primary (1°)



Secondary (2°)

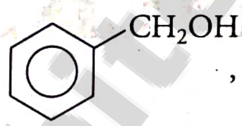


Tertiary (3°)

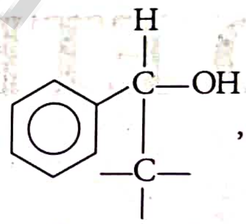
Benzylic Alcohols

In these alcohols, the —OH group is attached to a sp^3 hybridised benzylic carbon atom (i.e. carbon atom next to an aromatic ring).

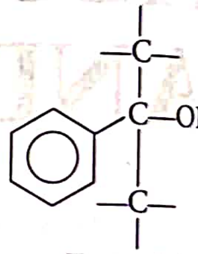
e.g.



Primary (1°)



Secondary (2°)



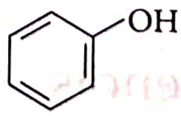
Tertiary (3°)

Compounds containing C_{sp^2}—OH Bond

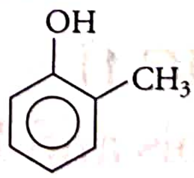
In these alcohols, the —OH group is attached to a carbon-carbon double bond, i.e. to a vinylic carbon ($CH_2=CH$—) or to an aryl carbon. These alcohols are also known as vinylic alcohols.

e.g. $CH_2=CH—OH$,

Vinylic alcohol



Phenol



2-methylphenol

NOMENCLATURE

For Alcohols

The common name of an alcohol is derived from common name of alkyl group and adding the word alcohol to it.

e.g. $CH_3OH \rightarrow \underbrace{CH_3 \text{ (methyl group)} + \text{alcohol}}_{\text{Methyl alcohol}}$

In IUPAC system, the name of an alcohol is derived from the name of the alkane from which the alcohol is derived, by replacing 'e' of alkane with the suffix 'ol'. The position of substituents are indicated by numerals.

Steps for writing the IUPAC name of the alcohols are as follows:

(i) Select the longest carbon chain (parent chain) containing —OH group.

(ii) The selected longest chain is numbered from the end nearest to the hydroxyl group.

(iii) Replace the 'e' of alkane by adding suffix 'ol'.

(iv) The positions of the —OH group and other substituents are indicated by using the numbers of carbon atoms to which these are attached.

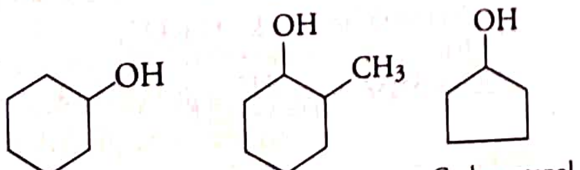
(v) For naming polyhydric alcohols, the 'e' of alkane is retained and the ending or suffix 'ol' is added.

(vi) Indicate the number of —OH groups by adding prefix like di, tri, etc., before 'ol'.

Common and IUPAC name of some alcohols

Compound	Common name	IUPAC name
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	*n*-propyl alcohol	Propan-1-ol
$CH_3-CH(OH)-CH_3$	*iso*-propyl alcohol	Propan-2-ol
$CH_3CH_2CH_2CH_2-OH$	*n*-butyl alcohol	Butan-1-ol
$CH_3-CH(OH)-CH_2-CH_3$	*sec*-butyl alcohol	Butan-2-ol
$CH_3-CH(CH_3)-CH_2OH$	*iso*-butyl alcohol	2-methyl propan-1-ol
$CH_3-C(CH_3)_2-OH$	*tert*-butyl alcohol	2-methyl propan-2-ol
$HOCH_2-CH(OH)-CH_2OH$	Glycerol	Propane-1, 2, 3-triol

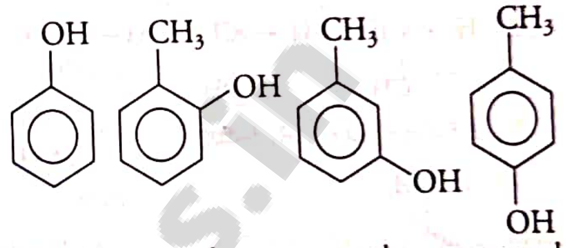
Cyclic alcohols are named using the prefix cyclo and considering the —OH group attached to C-1. e.g.



Cyclohexanol 2-methyl cyclohexanol Cyclopentanol

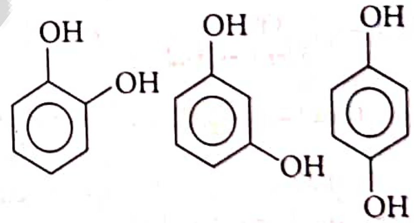
For Phenols

The name phenol is given to simplest hydroxy derivative of benzene and it is also an accepted IUPAC name. As the structure of phenol involves a benzene ring in its substituted compounds, the terms *ortho* (1, 2-disubstituted), *meta* (1,3-disubstituted) and *para* (1,4-disubstituted) are often used in the common names.



Common name	Phenol	*o*-cresol	*m*-cresol	*p*-cresol
IUPAC name	Phenol	2-methyl phenol	3-methyl phenol	4-methylphenol

Dihydroxy derivatives of benzene are known as 1,2, 1,3- and 1,4-benzenediol.

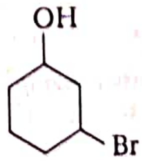


Common name	Catechol	Resorcinol	Quinol or Hydroquinone
IUPAC name	Benzene-1, 2-diol	Benzene-1, 3-diol	Benzene-1,4-diol

EXAMPLE |1| Name the following compounds according to IUPAC system.

(i) $CH_3-CH_2-CH(CH_2Cl)-CH(CH_2OH)-CH(CH_3)-CH_3$

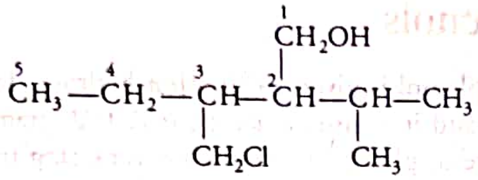
(ii) $CH_3-CH(CH_3)-CH_2-CH(OH)-CH(CH_2OH)-CH_3$

(iii) 

(iv) $H_2C=CH-CH(OH)-CH_2-CH_2-CH_3$

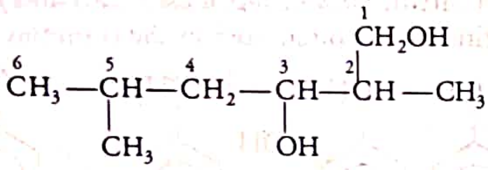
(v) $CH_3-C(CH_3)=C(Br)-CH_2OH$ **NCERT Intext**

Sol. (i)



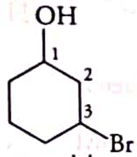
3-chloromethyl-2-isopropylpentan-1-ol

(ii)



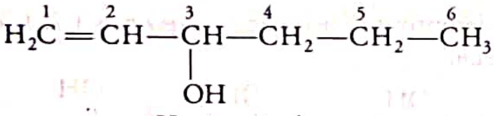
2, 5-dimethylhexan-1, 3-diol

(iii)



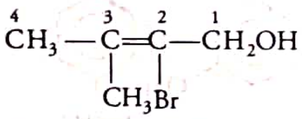
3-bromocyclohexanol

(iv)



Hex-1-en-3-ol

(v)

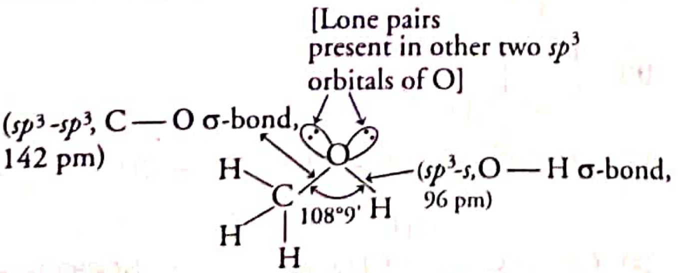


2-bromo-3-methylbut-2-en-1-ol

STRUCTURES OF FUNCTIONAL GROUPS (ALCOHOLS AND PHENOLS)

In alcohols, the oxygen atom of —OH group is attached to carbon atom by a σ (sigma) bond which is formed by overlapping of a sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital of oxygen.

In alcohols, the bond angle of C—$\ddot{\text{O}}$—H is 108° 9′. Due to the repulsion between the unshared electron pairs of oxygen, the bond angle in alcohols is lesser than the tetrahedral angle (109°28′).



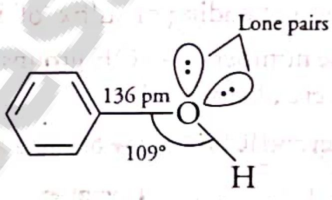
Structure of methanol

In phenols, the —OH group is attached to sp^2 hybridised carbon atom of aromatic ring. This C—O bond is formed by the overlapping of sp^3 orbital of oxygen with sp^2 hybridised orbital of carbon of benzene ring. The carbon-oxygen bond length (136 pm) in phenol is slightly less than that in methanol.

This is due to

(i) partial double bond character on account of the conjugation of unshared electron pairs of oxygen with the aromatic ring.

(ii) sp^2 hybridised state of carbon to which oxygen is attached.



Structure of phenol

METHODS OF PREPARATION

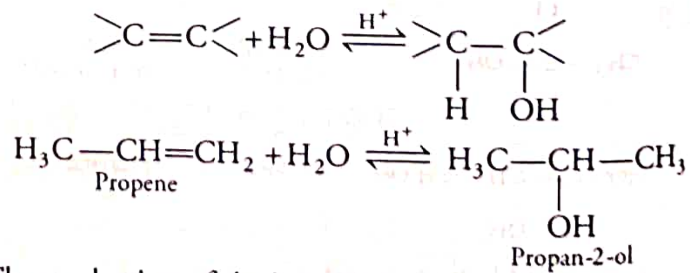
Preparation of Alcohols

These are prepared by the following methods:

From Alkenes

(i) By Acid Catalysed Hydration

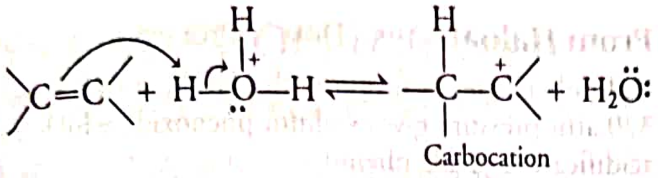
The term hydration refers to the addition of a molecule of water. Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition of water takes place in accordance with Markownikoff's rule. This rule states that negative part of the water molecule, i.e. OH^- part gets attached to that carbon atom which possesses lesser number of hydrogen atoms.



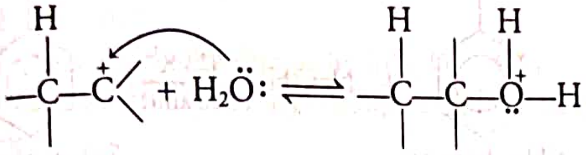
The mechanism of the hydration of alkene involves the following three steps:

Step I Protonation of alkene to form a stable carbocation by electrophilic attack of H_3O^+.

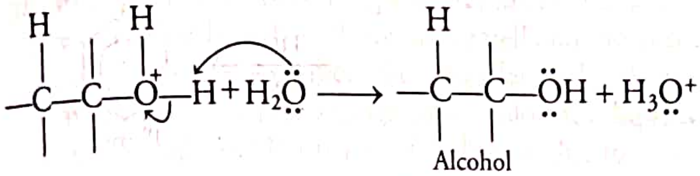
$$H_2O + \underset{\text{(From an acid)}}{H^+} \longrightarrow H_3O^+$$



Step II Nucleophilic attack of water on carbocation



Step III Deprotonation to form an alcohol



(ii) By Hydroboration-Oxidation

Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as addition product which upon subsequent oxidation by H_2O_2 in the presence of aqueous sodium hydroxide give alcohols.

$$\underset{\text{Propene}}{CH_3-CH{=}CH_2} + \underset{\text{Diborane}}{(H-BH_2)_2} \longrightarrow$$

$$CH_3-\underset{\displaystyle H}{\underset{|}{CH}}-\underset{\displaystyle BH_2}{\underset{|}{CH_2}} \xrightarrow{CH_3-CH=CH_2}$$

$$(CH_3-CH_2-CH_2)_2BH \xrightarrow{CH_3-CH=CH_2}$$

$$\underset{\text{Trialkylborane}}{(CH_3-CH_2-CH_2)_3B} \xrightarrow[3H_2O_2,\,\bar{O}H]{H_2O} B(OH)_3 + 3\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2-OH}$$

Here, the addition of borane to the double bond takes place in such a manner that the boron atom gets attached to the sp^2 carbon carrying greater number of hydrogen atoms. The alcohols seem to have been formed by the addition of water to the alkene in a way opposite to the Markovnikov's rule. In this reaction, alcohol is obtained in excellent yield.

From Carbonyl Compounds

(i) By the Reduction of Aldehydes and Ketones

Aldehydes and ketones are reduced to the corresponding alcohols by:

(i) addition of H_2 in the presence of a finely divided catalyst like Pt, Pd, Ni or Ru metals (catalytic hydrogenation).

$$R-CHO + H_2 \xrightarrow{Ni/Pd} R-CH_2OH$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + H_2 \xrightarrow{Ni/Pd} \underset{\text{Ethanol (1°)}}{CH_3CH_2OH}$$

(ii) complex metal hydrides such as $LiAlH_4$, $NaBH_4$, etc. Aldehydes yield primary alcohols whereas ketones give secondary alcohols.

$$\begin{matrix} R \\ R' \end{matrix}\!\!>C=O \xrightarrow{NaBH_4} \begin{matrix} R \\ R' \end{matrix}\!\!>CH-OH$$

$$\underset{\text{Aldehyde}}{R-CHO} \xrightarrow{LiAlH_4} \underset{1°\text{alcohol}}{R-CH_2OH}$$

$$\underset{\text{Acetone}}{\begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>C=O} \xrightarrow{LiAlH_4} \underset{\text{Propan-2-ol (2°)}}{\begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>CH-OH}$$

(ii) By the Reduction of Carboxylic Acids and Esters

Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride, a strong reducing agent.

$$R-COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4} RCH_2OH$$

$$C_6H_5-COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4} \underset{\text{Benzyl alcohol}}{C_6H_5-CH_2OH}$$

In this reaction, excellent yield of alcohols are obtained. However, $LiAlH_4$ is an expensive reagent and therefore, used for preparing special chemicals only.

Commercially, acids are reduced to alcohols by converting them to esters, which on catalytic hydrogenation usually at high temperature and pressure give a mixture of two alcohols.

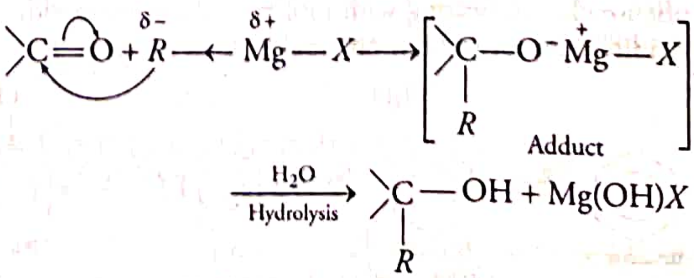
$$\underset{\text{Carboxylic acid}}{RCOOH} \xrightarrow[H^+]{R'OH} \underset{\text{Ester}}{RCOOR'} \xrightarrow[\text{Catalyst}]{H_2/\text{Copper chromite}} RCH_2OH + R'OH$$

From Grignard Reagents

Aldehydes and ketones react with Grignard reagent to form alcohol in two steps. These are as follows:

Step I This step involves the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct.

Step II This step involves the hydrolysis of an adduct to yield an alcohol.



The overall reactions using different aldehydes and ketones are as follows:

$$\underset{\text{Formaldehyde}}{HCHO} + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H_2O} \underset{1^\circ\text{ alcohol}}{RCH_2OH} + Mg(OH)X$$

$$RCHO + R'MgX \longrightarrow R{-}\overset{\displaystyle R'}{\overset{|}{C}}H{-}OMgX \xrightarrow{H_2O} \underset{2^\circ\text{ alcohol}}{R{-}\overset{\displaystyle R'}{\overset{|}{C}}H{-}OH} + Mg(OH)X$$

$$RCOR' + R''MgX \longrightarrow R{-}\overset{\displaystyle R'}{\overset{|}{\underset{\displaystyle R''}{\underset{|}{C}}}}{-}OMgX \xrightarrow{H_2O} \underset{3^\circ\text{ alcohol}}{R{-}\overset{\displaystyle R'}{\overset{|}{\underset{\displaystyle R''}{\underset{|}{C}}}}{-}OH} + Mg(OH)X$$

Only formaldehyde yields primary alcohol on reaction with Grignard reagents whereas all other aldehydes and ketones give secondary and tertiary alcohols, respectively.

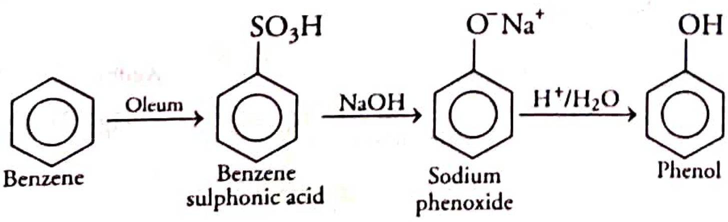
Preparation of Phenols

Phenols are also called **carbolic acid**. It was first isolated in the early 19th century from coaltar. Now a days, it is commercially produced synthetically. In the laboratory, phenols are prepared from benzene derivatives.

Phenols are prepared by the following methods:

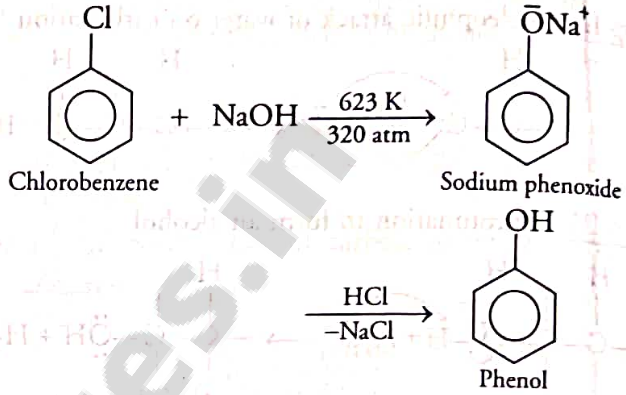
From Benzene Sulphonic Acid

When benzene is sulphonated with oleum ($H_2S_2O_7$ = conc. $H_2SO_4 + SO_3$), then benzene sulphonic acid is formed which gets further converted to sodium phenoxide, on heating with molten sodium hydroxide. Acidification of sodium phenoxide gives phenol.



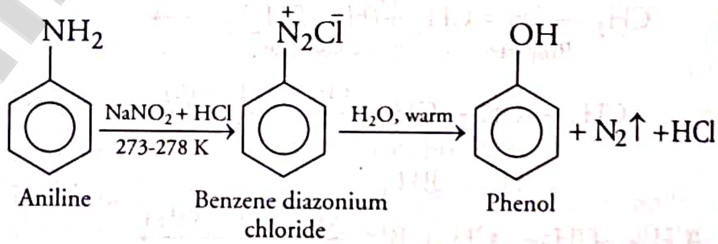
From Haloarenes (Dow's Process)

Chlorobenzene on fusion with NaOH at 623 K and 320 atm pressure gives sodium phenoxide which on acidification yields phenol.



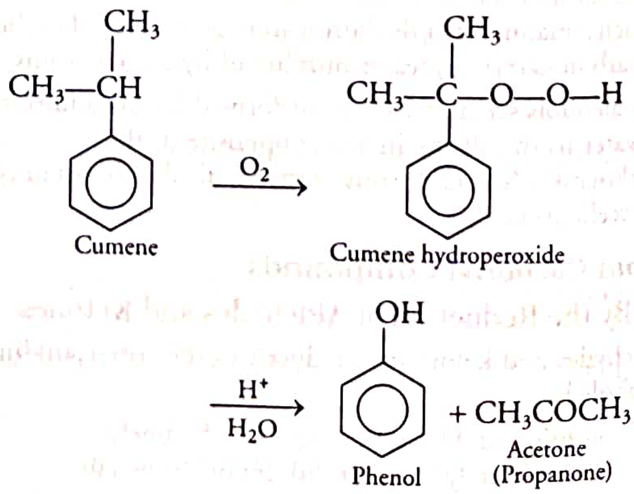
From Diazonium Salts

A diazonium salt of aromatic amine (i.e. aniline) is formed by treating amine with nitrous acid ($NaNO_2$ + HCl) at 273 K-278 K. Diazonium salts on hydrolysis with warm water or dilute acids give phenols.



From Cumene

Cumene (*iso*-propyl benzene) on aerial oxidation form cumene hydroperoxide which upon subsequent hydrolysis with dilute acid gives phenol and propanone (acetone). Acetone (a by-product) is obtained in large quantities.



Note Most of the world wide production of phenol is from cumene.

PHYSICAL PROPERTIES OF ALCOHOLS AND PHENOLS

The alcohols and phenols consist of two parts:

(i) Alkyl or aryl group and

(ii) Hydroxyl group

Their properties are chiefly due to hydroxyl (—OH) group. The nature of alkyl or aryl groups simply modify these properties.

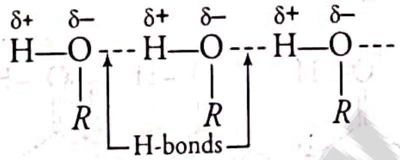
Some important physical properties are as follows :

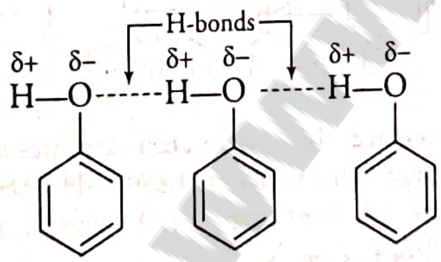
(i) **Physical state** At room temperature, lower alcohols are colourless liquids with distinct smell and burning taste. The higher members are colourless, odourless waxy solids. Pure phenols are either colourless liquids or solids and usually turn reddish-brown due to atmospheric oxidation.

(ii) **Boiling points** The boiling points of alcohols and phenols increase with increase in number of C-atoms (due to increase in van der Waals' forces).

In alcohols, the boiling point decreases with increase of branching in carbon chain because of decrease in van der Waals' forces with decrease in surface area.

The —OH group in alcohols and phenols is involved in intermolecular hydrogen bonding or H-bonding due to which they exist as associated molecules and hence, have higher boiling points.



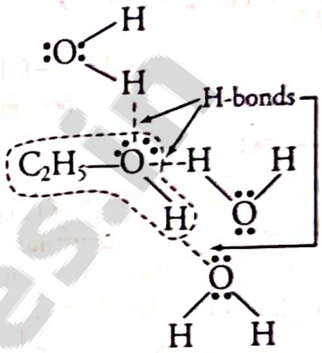


Boiling points of alcohols and phenols are usually higher in comparison to hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. This is mainly due to the presence of intermolecular H-bonding in them which is absent in ethers and hydrocarbons.

C_2H_5OH	CH_3OCH_3
Ethanol	Methoxy methane
Molecular mass = 46	Molecular mass = 46
Boiling point = 351 K	Boiling point = 248 K

$CH_3CH_2CH_3$
Propane
Molecular mass = 44
Boiling point = 231 K

(iii) **Solubility** The solubility of alcohols and phenols in water is due to their ability to form H-bonds with water molecules. Solubility decreases with increase in size of alkyl/aryl (i.e. hydrophobic) groups. However, solubility of isomeric alcohols increases with branching due to decrease in surface area of hydrophobic part. Many lower molecular mass alcohols are miscible with water in all proportions.



H-bonding between alcohol and water molecules

CHEMICAL REACTIONS OF ALCOHOLS AND PHENOLS

Alcohols are versatile compounds. They react both as nucleophiles and electrophiles in the following manner.

(i) The bond between O—H is broken when alcohol reacts as nucleophiles.

$$R-\ddot{O}-H + \rangle C^+ \longrightarrow R-\overset{+}{O}(H)-\overset{|}{\underset{|}{C}}- \longrightarrow R-O-\overset{|}{\underset{|}{C}}- + H^+$$

(ii) The bond between C—O is broken when alcohols react as electrophiles.

$$R-CH_2-OH + H^+ \longrightarrow RCH_2-\overset{+}{O}H_2 \xrightarrow{Br^-} Br-\underset{R}{CH_2} + H_2O$$

Based on the cleavage of O—H and C—O bonds, the reactions of alcohols and phenols may be divided into following two groups :

(a) Reactions Involving Cleavage of O—H Bond

Some typical reactions of alcohols and phenols involving the cleavage of O—H bond are as follows:

Acidity of Alcohols and Phenols

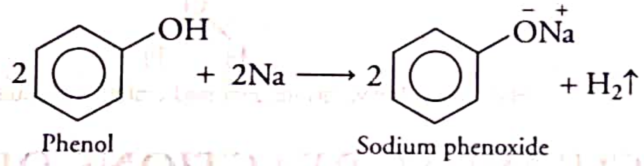
Reaction with Metals

Alcohols and phenols react with active metals like Na, K, Al to produce corresponding alkoxides or phenoxides with the evolution of hydrogen gas.

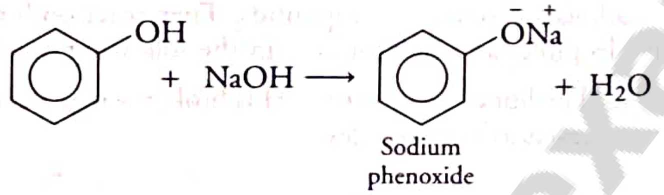
$$2R\text{—O—H} + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2R\text{—}\overset{-}{O}\overset{+}{Na}} + H_2\uparrow$$

$$\underset{\text{Ethyl alcohol}}{2CH_3\text{—}CH_2\text{—}OH} + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2CH_3\text{—}CH_2\text{—}\overset{-}{O}\overset{+}{Na}} + H_2\uparrow$$

$$\underset{tert\text{-butyl alcohol}}{6(CH_3)_3C\text{—}OH} + 2Al \longrightarrow \underset{\text{Aluminium } tert\text{-butoxide}}{2[(CH_3)_3CO)]_3Al} + 3H_2\uparrow$$



In addition to this, phenols react with aqueous NaOH to form sodium phenoxides.



All the above reactions show that alcohols and phenols are acidic in nature. Actually, alcohols and phenols are Bronsted acids, i.e. they can donate a proton to a stronger base ($\ddot{B}$:).

$$\underset{\text{Base}}{\ddot{B}:} + \underset{\text{Acid}}{H\text{—}\ddot{\underset{\cdot\cdot}{O}}\text{—}R} \longrightarrow \underset{\text{Conjugate acid}}{B\text{—}H} + \underset{\text{Conjugate base}}{:\overset{-}{\ddot{\underset{\cdot\cdot}{O}}}\text{—}R}$$

Acidity of Alcohols

Polar nature of O—H bond is responsible for the acidic nature of alcohols. An electron releasing group (alkyl group) increases electron density on oxygen tending to decrease the polarity of O—H bond, which decreases their acidic strength. Thus, acidity of alcohols decreases in the following order:

$$\underset{(1^\circ\text{alcohol})}{R\rightarrow CH_2\text{—}OH} > \underset{(2^\circ\text{ alcohol})}{\begin{matrix}R\searrow\\R'\nearrow\end{matrix}CH\text{—}OH} >> \underset{(3^\circ\text{ alcohol})}{\begin{matrix}R\\R'\rightarrow\\R''\nearrow\end{matrix}C\text{—}OH}$$

However, alcohols are weaker acids than water. Water is a better proton donor than alcohol. This can be illustrated by the reaction of water with an alkoxide.

Conversely, alkoxide ion is a better proton acceptor than hydroxide ion. In other words, alkoxides are stronger bases than hydroxide ion, i.e. sodium ethoxide is a stronger base than sodium hydroxide.

$$\underset{\text{Base}}{R\text{—}\overset{-}{\ddot{\underset{\cdot\cdot}{O}}}:} + \underset{\text{Acid}}{H\text{—}\ddot{\underset{\cdot\cdot}{O}}\text{—}H} \longrightarrow \underset{\text{Conjugate acid}}{R\text{—}O\text{—}H} + \underset{\text{Conjugate base}}{:\ddot{\underset{\cdot\cdot}{O}}H^-}$$

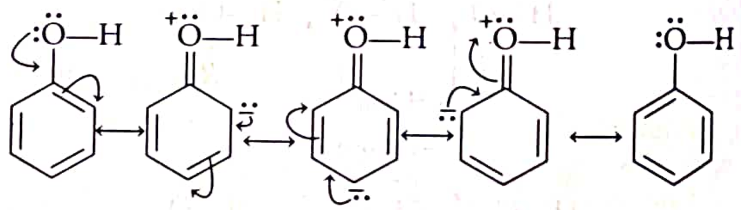
In the presence of strong acids, alcohols act as Bronsted bases because they can accept a proton from strong acids to form protonated alcohols. It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

$$\underset{\text{Base}}{R\text{—}\ddot{\underset{\cdot\cdot}{O}}\text{—}H} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow \underset{\text{Protonated alcohol}}{R\text{—}\overset{+}{\underset{\cdot\cdot}{O}}\begin{matrix}H\\H\end{matrix}} + HSO_4^-$$

Acidity of Phenols

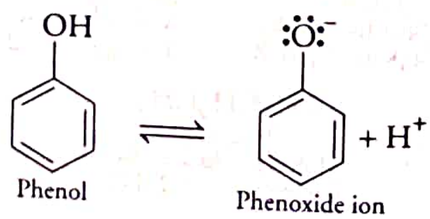
The reactions of phenol with metals such as Na, Al and sodium hydroxide indicate its acidic nature. In phenol, —OH group is directly attached to sp^2 hybridised carbon of benzene ring which acts as electron withdrawing group.

Due to this, the lone pairs of electrons of —OH are involved in resonance with C-atom of benzene ring. This delocalisation of electrons (or resonance) can be represented as:



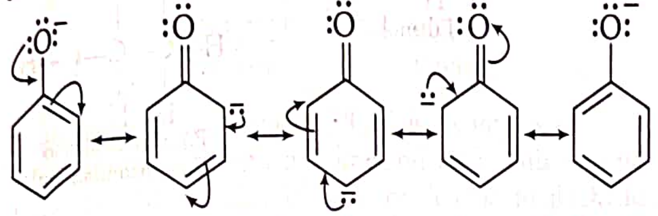
Due to resonance, the oxygen atom acquires a partial positive charge. This weakens the O—H bond and thus facilitates the release of a proton. As a result, phenols behave as Bronsted acids. The reaction of phenol with aqueous NaOH indicates that phenols are stronger acids than alcohols. It is because the phenoxide ion left after the release of a proton is stabilised by resonance but not the alkoxide ion.

$$\underset{\text{Alcohol}}{R\text{—}\ddot{\underset{\cdot\cdot}{O}}\text{—}H} \rightleftharpoons \underset{\substack{\text{Alkoxide ion}\\\text{(not stabilised by resonance)}}}{R\text{—}\ddot{\underset{\cdot\cdot}{O}}:^-} + H^+$$

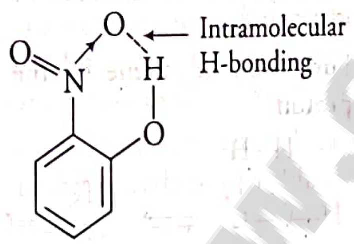


Resonance in Alkoxide and Phenoxide Ions

In alkoxide ion, the negative charge is localised on oxygen while in phenoxide ion, the charge is delocalised. The delocalisation of negative charge makes phenoxide ion more stable and favours the ionisation of phenol. However, phenol is less stable than phenoxide ion because its resonance structures have charge separation. Phenoxide ion exists as a resonance hybrid of the following structures:



In substituted phenols, presence of electron withdrawing groups such as —NO_2 group increases the acidic strength of phenol. All nitrophenols are more acidic than phenol. This effect is more pronounced when —NO_2 group (electron withdrawing group) is present at *ortho* and *para* positions. Therefore, *ortho* and *para*-nitrophenols are more acidic than *meta*-nitrophenol. It is due to the effective delocalisation of negative charge in phenoxide ion. *o*-nitrophenol is slightly less acidic than *p*-nitrophenol due to intramolecular H-bonding which makes loss of a proton more difficult.



Presence of electron releasing groups such as alkyl groups in substituted phenols do not favour the formation of phenoxide ion resulting in decreasing the acidic strength. That's why, cresols are less acidic than phenol. Further, greater the number of electron withdrawing group at *o*- and *p*-positions, more acidic is phenol.

pK_a values of some phenols and ethanol

Compound	Formula	pK_a
o-nitrophenol	o-$O_2N-C_6H_4-OH$	7.2
m-nitrophenol	m-$O_2N-C_6H_4-OH$	8.3
p-nitrophenol	p-$O_2N-C_6H_4-OH$	7.1
Phenol	C_6H_5-OH	10.0
o-cresol	o-$CH_3-C_6H_4-OH$	10.2
m-cresol	m-$CH_3-C_6H_4-OH$	10.1
p-cresol	p-$CH_3-C_6H_4-OH$	10.2
Ethanol	C_2H_5OH	15.9

Note From the above table, it is clear that phenol is million times more acidic than ethanol.

Esterification

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.
(R' = alkyl or aryl group)

$$\underset{\text{Carboxylic acid}}{R\text{—COOH}} + \underset{\text{Alcohol}}{R'\text{—OH}} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R\text{—COOR}'} + H_2O$$

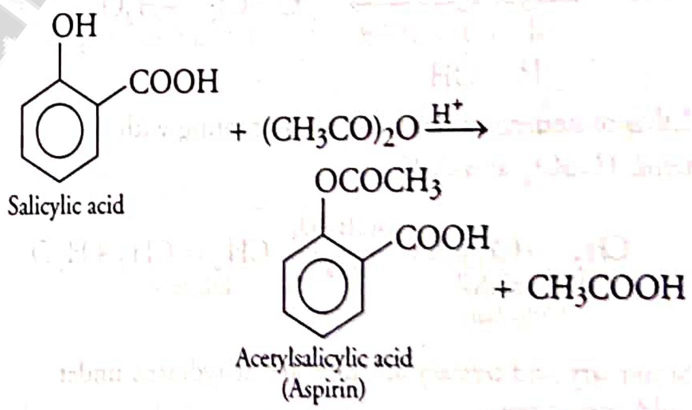
$$\underset{\text{Acid anhydride}}{(R\text{—CO})_2O} + R'\text{—OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R\text{—COOR}'} + R\text{—COOH}$$

Both the above reactions are carried out in the presence of conc. H_2SO_4. The reaction is reversible and hence water is removed as soon as it is formed.

Reaction with acid chloride is carried out in the presence of pyridine (base) so as to neutralise HCl which is formed during the reaction. It shifts the equilibrium towards right hand side.

$$\underset{\text{Acyl chloride}}{R\text{—COCl}} + \underset{\text{Alcohol}}{R'\text{—OH}} \xrightarrow{\text{Pyridine}} \underset{\text{Ester}}{R\text{—COOR}'} + HCl$$

The introduction of acetyl (CH_3CO—) group in alcohols or phenols is known as **acetylation**. **Acetylation** of salicylic acid produces aspirin.



Note Aspirin possesses analgesic, anti-inflammatory and antipyretic properties.

(b) Reactions Involving Cleavage of (C—O) Bond

The reactions involving cleavage of C—O bond takes place only in alcohols. Phenols show this type of reaction only with Zn.

Reaction with Hydrogen Halides

Alcohols react with hydrogen halides to form alkyl halides.

$$\underset{\text{Alcohol}}{R\text{—OH}} + H\text{—}X \longrightarrow \underset{\text{Alkyl halide}}{R\text{—}X} + H_2O$$

$$\underset{\text{Ethanol}}{C_2H_5OH} + HCl \xrightarrow[ZnCl_2]{\text{Anhydrous}} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + H_2O$$

The difference in reactivity of three classes of alcohols with conc. HCl distinguishes them from one another. This is called **Lucas test.**

Alcohols are soluble in Lucas reagent (conc. $HCl + ZnCl_2$) while their halides are immiscible and produce turbidity in solution. Tertiary alcohols produce turbidity immediately as they form halides easily. Secondary alcohols produce turbidity after 5 minutes, while primary alcohols do not produce turbidity at room temperature.

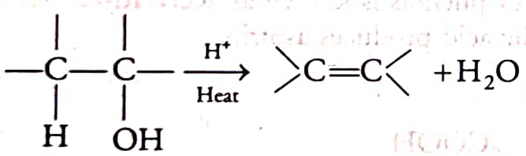
Reaction with Phosphorus Trihalides

Alcohols are converted to alkyl halides by reaction with phosphorus trihalides.

$$3R{-}OH + PX_3 \longrightarrow 3R{-}X + H_3PO_3 \;(X = Cl, Br)$$

Dehydration

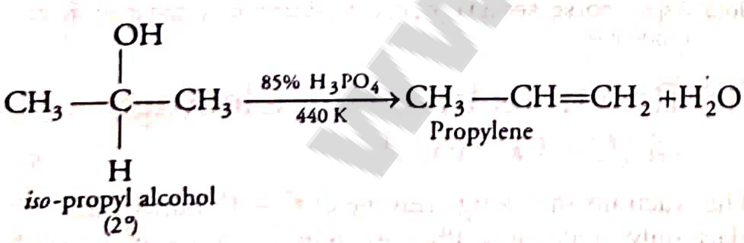
Alcohols undergo dehydration (i.e. removal of a molecule of water) to form alkenes on treatment with a protic acid such as H_2SO_4 or H_3PO_4 or catalysts such as anhydrous $ZnCl_2$ or Al_2O_3.

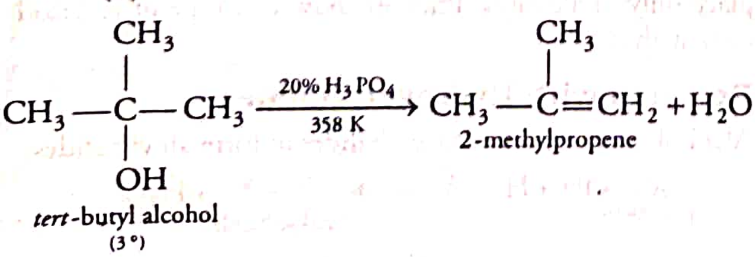


Ethanol undergoes dehydration by heating with conc. H_2SO_4 at 443 K

$$\underset{\substack{\text{Ethyl alcohol}\\(1^\circ\text{alcohol})}}{CH_3{-}CH_2OH} \xrightarrow[443\,K]{Conc.\,H_2SO_4} \underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2O$$

Secondary and tertiary alcohols are dehydrated under mild conditions,





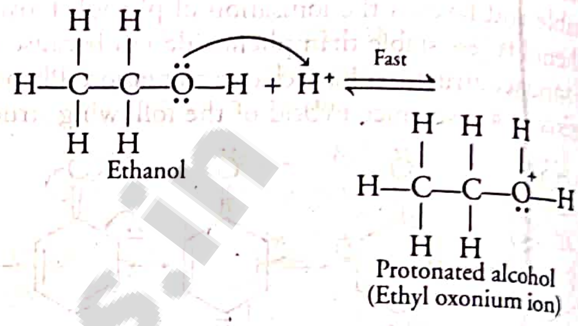
Order for ease of dehydration is:

3° alcohol > 2° alcohol > 1° alcohol.

Mechanism

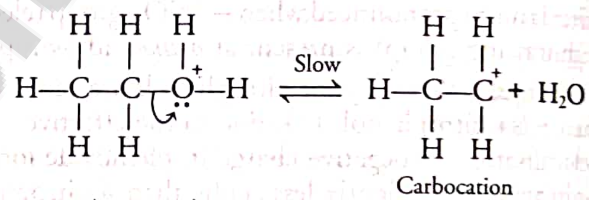
The mechanism of dehydration of ethanol involves the following steps:

<u>*Step I*</u> **Formation of protonated alcohol**



<u>*Step II*</u> **Formation of carbocation**

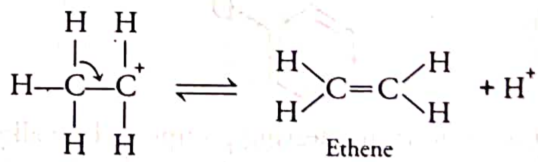
It is the slowest step and hence, it is the rate determining step of the reaction.



Note

Tertiary carbocations are more stable and therefore, are easier to form than secondary and primary carbocations. Tertiary alcohols are the easiest to dehydrate.

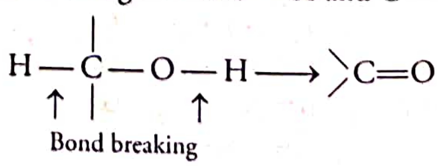
<u>*Step III*</u> **Formation of ethene by the elimination of a proton**



The acid used in step I is released in step III. To drive the equilibrium to the right, ethene is removed as it is formed.

Oxidation

Oxidation of alcohols involves the formation of C=O bond with the cleavage of an O—H and C—H bonds.



This reaction involves the loss of H_2 molecule from an alcohol molecule, therefore these reactions are known as **dehydrogenation reactions.** Depending upon the oxidising agent used, a primary alcohol is oxidised to an aldehyde which in turn is oxidised to a carboxylic acid.

$$CH_3—CH_2—OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{Acetaldehyde}}{CH_3CH{=}O} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$
Ethanol

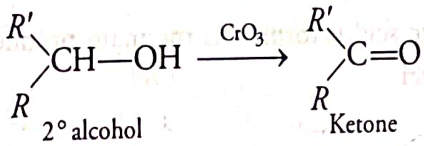
Strong oxidising agents are used to get carboxylic acids from alcohols directly. CrO_3 in anhydrous medium is used as an oxidising agent for the isolation of aldehydes.

$$\underset{1^\circ\text{ alcohol}}{RCH_2OH} \xrightarrow{CrO_3} \underset{\text{Aldehyde}}{RCHO}$$

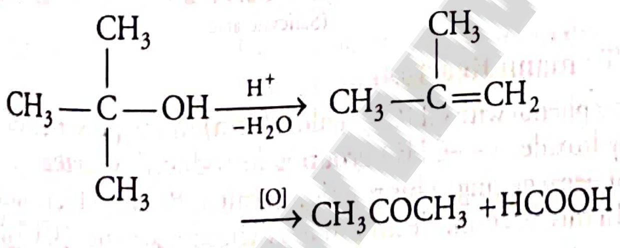
Pyridinium chlorochromate (PCC) is a complex of chromium trioxide with pyridine and HCl. This reagent is used for the oxidation of primary alcohols to aldehydes.

$$CH_3—CH{=}CH—CH_2OH \xrightarrow{PCC} CH_3—CH{=}CH—CHO$$

Secondary alcohols are oxidised to ketones by chromic anhydride (CrO_3).



3° alcohols do not undergo oxidation reaction. But in the presence of strong oxidising agents such as acidified $K_2Cr_2O_7$ and acidified $KMnO_4$ and at elevated temperatures, cleavage of various C—C bonds takes place. As a result, a mixture of ketone and an acid, each containing lesser number of carbon atoms than the original alcohol is obtained.

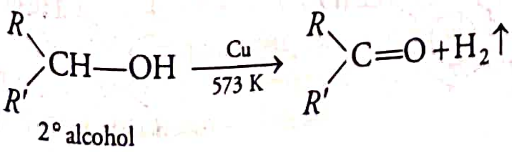


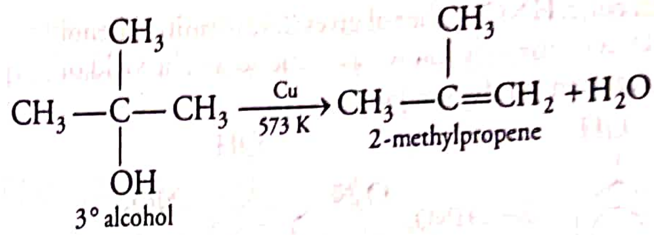
$$HCOOH \xrightarrow{[O]} H_2O + CO_2\uparrow$$

Action of Heated Copper

When the vapours of a primary or secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed while tertiary alcohols undergo dehydration to form alkenes.

$$\underset{1^\circ\text{ alcohol}}{R—CH_2—OH} \xrightarrow[573\text{ K}]{Cu} \underset{\text{Aldehyde}}{R—CHO} + H_2\uparrow$$





Note Reactions of alcohol with copper are also used to distinguish between primary, secondary and tertiary alcohols.

Exclusive Reactions of Phenols

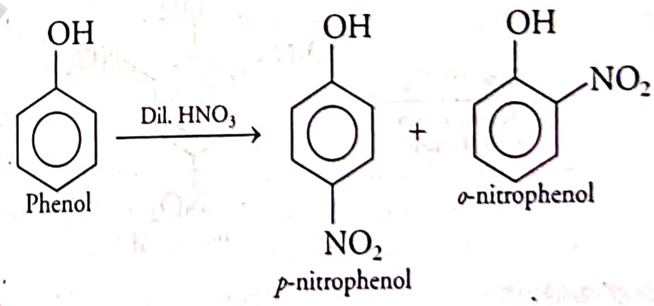
Following reactions are shown by phenols only:

Electrophilic Aromatic Substitution

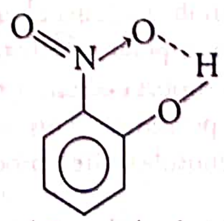
Phenols undergo electrophilic aromatic substitution reaction readily because —OH group attached to the benzene ring activates the benzene ring towards electrophilic substitution. Further, it directs the incoming group to *ortho* and *para* positions in the ring as these positions become electron rich due to the resonance effect. Common electrophilic aromatic substitution reactions taking place in phenol are:

(a) Nitration

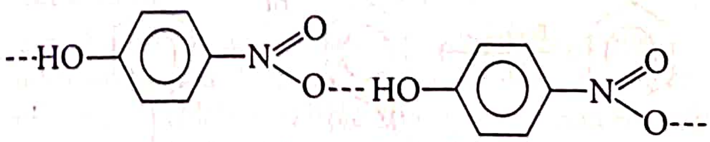
With dilute HNO_3 at low temperature, i.e. 298K, phenol yields a mixture of *ortho* and *para* nitrophenols.



The *ortho* and *para* isomers can be separated by steam distillation. *o*-nitrophenol is steam volatile due to intramolecular H-bonding while *p*-nitrophenol is less volatile due to association of molecules by intermolecular H-bonding.

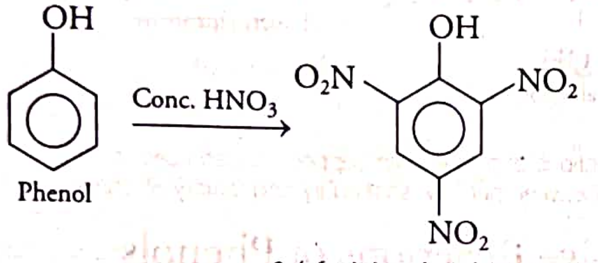


o-nitrophenol (Intramolecular H-bonding)



p-nitrophenol (Intermolecular H-bonding)

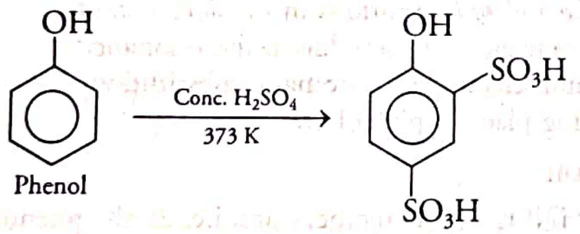
With conc. HNO_3, phenol gives 2,4,6-trinitrophenol which is commonly known as picric acid. The yield of the reaction product is poor.



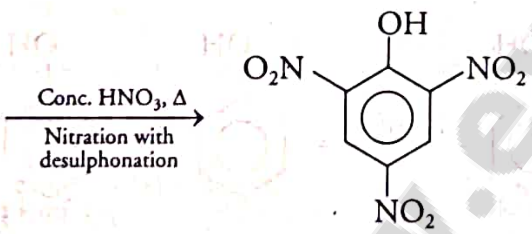
2,4,6-trinitrophenol (Picric acid)

Note 2,4,6-trinitrophenol is a strong acid due to the presence of three electron withdrawing $-NO_2$ groups which facilitate the release of hydrogen ion.

Now a days, picric acid is prepared by first treating phenol with conc. H_2SO_4 at 373 K to form phenol-2,4-disulphonic acid and then with conc. HNO_3 to get picric acid.



Phenol-2,4-disulphonic acid

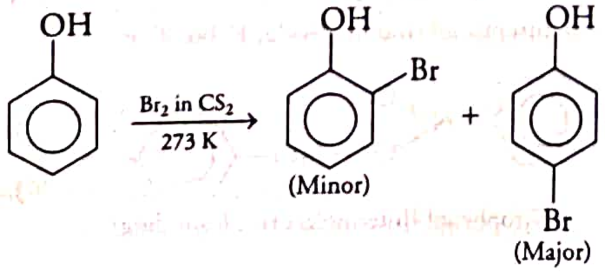


Picric acid

Halogenation

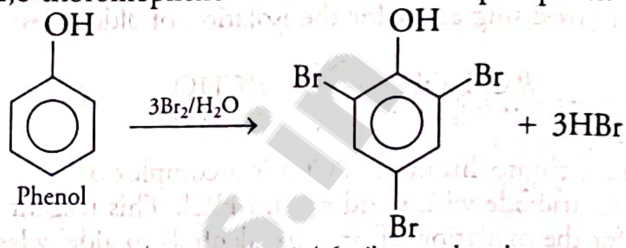
When phenol is treated with bromine, different reaction products are formed under different experimental conditions. These are as follows:

- When bromination is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 at low temperature, monobromophenols are formed. In the presence of non-polar solvents, ionisation of phenol is greatly suppressed and ring is activated slightly at 1,4 positions. This results in the formation of monosubstituted product only.



Usually, halogenation of benzene is carried out in the presence of Lewis acid which polarises the halogen molecule. But in case of phenol, polarisation of Br_2 molecule takes place even in the absence of Lewis acid because of the highly activating effect of —OH group.

- When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.

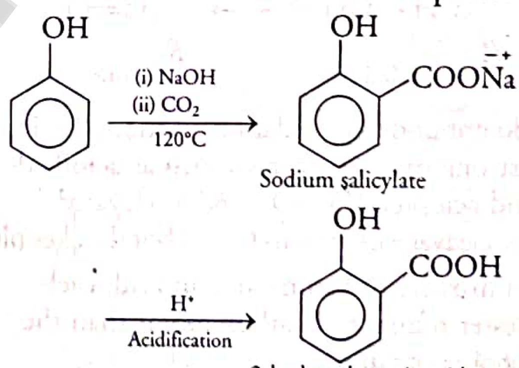


2,4,6-tribromophenol (White ppt)

Kolbe's Reaction

Phenoxide ion produced by treating phenol with NaOH is more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with weak electrophile, CO_2.

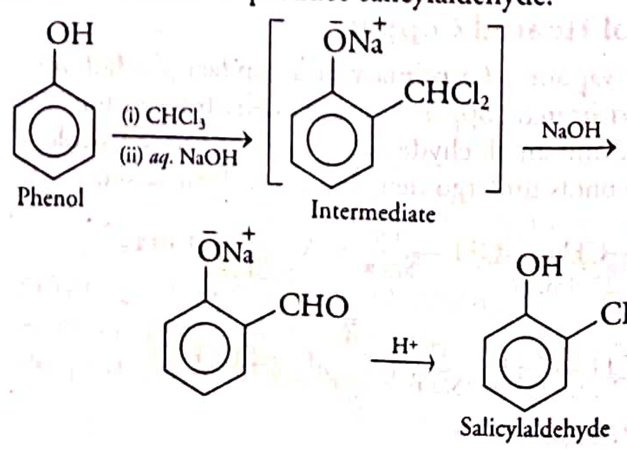
o-hydroxybenzoic acid is formed as the main product.



2-hydroxybenzoic acid (Salicylic acid)

Reimer-Tiemann Reaction

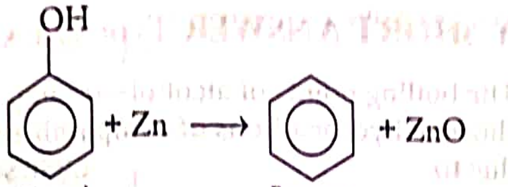
On treating phenol with $CHCl_3$ (chloroform) in the presence of sodium hydroxide, a —CHO group is introduced at *ortho* position of benzene ring. This reaction is called Reimer-Tiemann reaction. In this reaction, electrophile is dichlorocarbene ($:CCl_2$). The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce salicylaldehyde.



Salicylaldehyde

Reaction of Phenol with Zinc Dust

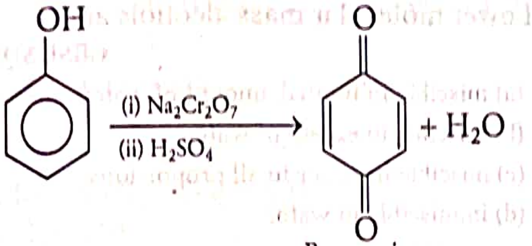
Phenol is converted to benzene on heating with zinc dust.



Phenol Benzene

Oxidation

Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone.



Benzoquinone

In the presence of air, phenol undergoes oxidation and gives dark-coloured mixtures containing quinones.

USES OF PHENOLS

Phenols are used as an antiseptic and disinfectant in soaps, in making of drugs, azo dyes, as a preservative for inks, in the manufacturing of picric acid which is used as an explosive.

SOME COMMERCIALLY IMPORTANT ALCOHOLS

Methanol and ethanol are some of the commercially important alcohols. These are discussed below:

(a) Methanol (CH_3OH)

It is also known as 'wood spirit', as it was produced by the destructive distillation of wood.

Preparation

Now-a-days, methanol is produced by the catalytic hydrogenation of carbon monoxide at high pressure and temperature in the presence of $ZnO - Cr_2O_3$ catalyst.

$$CO + 2H_2 \xrightarrow[\substack{200-300\ \text{atm} \\ 575-673\ \text{K}}]{ZnO\text{-}Cr_2O_3} \underset{\text{Methyl alcohol or methanol}}{CH_3—OH}$$

Properties

Methanol is a colourless liquid with a boiling point of 337 K. It is highly poisonous in nature and ingestion of even small quantities of methanol can cause blindness and large quantities cause even death.

Uses

It is used as a solvent in paints, varnishes and in formaldehyde formation, as an antioxidant.

(b) Ethanol (C_2H_5OH)

Ethanol is a volatile, flammable, colourless liquid having chemical formula C_2H_5OH.

Preparation

It is obtained commercially by the fermentation of sugar present in molasses, sugarcane or fruits like grapes.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\substack{\text{Glucose} \\ \text{or Fructose}}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2\uparrow$$

Fermentation takes place in anaerobic conditions, i.e. in the absence of air. Carbon dioxide is released during fermentation. If air gets into fermentation mixture, the oxygen of air oxidises ethanol to ethanoic acid which destroys the taste of alcoholic drinks.

Properties

It is a colourless liquid with boiling point of 351 K. It is harmful for central nervous system. It can affect judgement, can cause nausea, loss of consciousness and can be fatal.

Uses

It is used as a solvent in paint industry and in wine making. 100% ethanol is called absolute alcohol. Commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol. Now a days, large quantities of ethanol are obtained by the hydration of ethene.

Note Absolute alcohol is 100% ethanol that is prepared from rectified spirit (ethanol) by azeotropic distillation.

Physiological Effect of Methanol and Ethanol

Many times alcoholic drink ethanol is mixed with methanol (denatured alcohol) that can cause blindness and death. In the body, methanol is oxidised first to methanal and then to methanoic acid.

The affected patient is treated by giving intravenous infusions of diluted ethanol. The enzyme responsible for oxidation of aldehyde (HCHO) to acid is swamped that gives time to kidneys to excrete methanol.

TOPIC PRACTICE 1

OBJECTIVE Type Questions

1. Which of the following alcohol contains C_{sp^3}—OH bond?

(a) Allylic alcohol (b) Vinylic alcohol
(c) Phenols (d) None of these

2. Give IUPAC name of the compound given below.

$$CH_3—\underset{\underset{Cl}{|}}{CH}—CH_2—CH_2—\underset{\underset{OH}{|}}{CH}—CH_3$$

NCERT Exemplar

(a) 2-chloro-5-hydroxyhexane
(b) 2-hydroxy-5-chlorohexane
(c) 5-chlorohexan-2-ol
(d) 2-chlorohexan-5-ol

3. IUPAC name of *m*-cresol is .... **NCERT Exemplar**

(a) 3-methylphenol
(b) 3-chlorophenol
(c) 3-methoxyphenol
(d) benzene-1, 3-diol

4. How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature? **NCERT Exemplar**

(a) 1 (b) 2 (c) 3 (d) 4

5. CH_3CONH_2 on reaction with NaOH and Br_2 in alcoholic medium gives **Delhi 2020**

(a) $CH_3CH_2NH_2$ (b) CH_3CH_2Br
(c) CH_3NH_2 (d) CH_3COONa

6. The process of converting alkyl halides into alcohols involves .... **NCERT Exemplar**

(a) addition reaction
(b) substitution reaction
(c) dehydrohalogenation reaction
(d) rearrangement reaction

7. Phenol is less acidic than .... **NCERT Exemplar**

(a) ethanol (b) *o* - nitrophenol
(c) *o* - methylphenol (d) *o* - methoxyphenol

8. CH_3CH_2OH can be converted into CH_3CHO by .... **NCERT Exemplar**

(a) catalytic hydrogenation
(b) treatment with $LiAlH_4$
(c) treatment with pyridinium chlorochromate
(d) treatment with $KMnO_4$

VERY SHORT ANSWER Type Questions

9. The boiling points of alcohols are higher than those of hydrocarbons of comparable masses due to **CBSE SQP (Term I)**

(a) hydrogen bonding
(b) ion – dipole interaction
(c) dipole- dipole interaction
(d) van der Waals' forces

10. Lower molecular mass alcohols are **CBSE SQP (Term I)**

(a) miscible in limited amount of water
(b) miscible in excess of water
(c) miscible in water in all proportions
(d) immiscible in water

11. Phenol does not undergo nucleophilic substitution reaction easily due to **CBSE SQP (Term I)**

(a) acidic nature of phenol
(b) partial double bond character of C—OH bond
(c) partial double bond character of C—C bond
(d) instability of phenoxide ion

12. What would be the reactant and reagent used to obtain 2, 4-dimethyl pentan-3-ol? **CBSE SQP (Term I)**

(a) Propanal and propyl magnesium bromide
(b) 3-methylbutanal and 2-methyl magnesium iodide
(c) 2-dimethylpropanone and methyl magnesium iodide
(d) 2-methylpropanal and *iso*-propyl magnesium iodide

13. *o*-hydroxy benzyl alcohol when reacted with PCl_3 given the product as (IUPAC name) **CBSE SQP (Term I)**

(a) *o*-hydroxy benzyl chloride
(b) 2-chloromethylphenol
(c) *o*-chloromethylchlorobenzene
(d) 4-hydroxymethylphenol

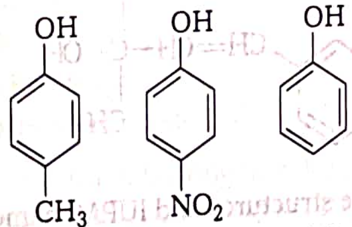
14. Which of the following reagents will not convert ethyl alcohol into ethyl chloride? **CBSE 2021 (Term I)**

(a) PCl_5
(b) NaCl
(c) $SOCl_2$
(d) $HCl / ZnCl_2$

15. Phenol on being heated with concentrated H_2SO_4 and then with concentrated HNO_3 gives **CBSE 2021 (Term I)**
(a) *o*-nitrophenol
(b) 2, 4, 6-trinitrophenol
(c) *p*-nitrophenol
(d) *m*-nitrophenol

16. A compond (*X*) with the molecular formula C_3H_8O can be oxidised to another compound (*Y*) whose molecular formula is $C_3H_6O_2$. The compound (*X*) may be **CBSE 2021 (Term I)**
(a) $CH_3CH_2—O—CH_3$
(b) $CH_3—\underset{\underset{OH}{|}}{CH}—CH_3$
(c) $CH_3—CH_2—CH_2—OH$
(d) $CH_3—CH_2—CHO$

17. Arrange the following compounds in decreasing order of their acidic character **CBSE 2021 (Term I)**



(I) (II) (III)

(a) II > I > III
(b) II > III > I
(c) III > I > II
(d) I > II > III

18. Write the IUPAC name of the following compound.

$$H_3C—\underset{\underset{CH_3}{|}}{C}=\underset{\underset{Br}{|}}{C}—CH_2—OH$$

All India 2017

19. Name the alcohol that is used to make the following ester:

$$CH_3—\overset{\overset{O}{||}}{C}—O—\underset{\underset{CH_3}{|}}{CH}—CH_3$$

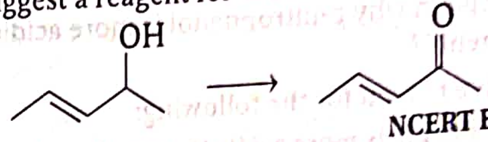
All India 2014 C

20. Of the two hydroxy organic compounds, *R*OH and *R*′OH, the first one is basic and other one is acidic in behaviour. How is *R* different from *R*′? **Delhi 2013**

21. Give the order of dehydration for primary, secondary and tertiary alcohols.

22. Why do phenols not give the protonation reaction readily? **All India 2008**

23. Suggest a reagent for the following conversion:



NCERT Exemplar

24. Write the equations involved in the Reimer-Tiemann reaction. **All India 2019, 2013; Delhi 2014**

SHORT ANSWER Type I Questions

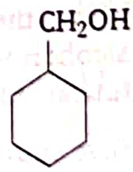
25. Give reason:
Phenols boil at higher temperature than haloarenes of comparable molecular mass.

26. Both methanol and phenol have an —OH group but the dipole moment of methanol (1.71 D) is higher than that of phenol (1.54 D). Why?

27. How will you convert
(i) propene to propan-1-ol?
(ii) ethanal to propan-2-ol? **Delhi 2013**

28. How do you convert the following?
(i) Propan-2-ol to 2-methylpropan-2-ol
(ii) Aniline to phenol **Delhi 2015**

29. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal?

(i) $CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_2OH$ (ii) 

All India 2019, NCERT Intext

30. When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place: **CBSE SQP 2021**

$$CH_3—\underset{\underset{CH_3}{|}}{CH}—\underset{\underset{OH}{|}}{CH}—CH_3 \xrightarrow{HBr} CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}—CH_2—CH_3$$

Give a mechanism for this reaction.

31. Out of 2-chloroethanol and ethanol, which one is more acidic and why? **NCERT Exemplar**

32. Explain why is *ortho*-nitrophenol more acidic than *ortho*-methoxyphenol? **NCERT; All India 2012**

33. *Ortho* and *para*-nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions. **NCERT Intext**

Or Explain why *p*-nitrophenol is more acidic than phenol?

34. Give reason for the following:
(i) Phenol is more acidic than methanol.
(ii) The C — O — H bond angle in alcohols is slightly less than the tetrahedral angle (109° 28′). **All India 2015**

35. (i) Arrange the following compounds in the increasing order of their acidic strength :
p-cresol, *p*-nitrophenol, phenol
(ii) Write the mechanism (using curved arrow notation) of the following reaction.

$$CH_2 = CH_2 \xrightarrow{H_3O^+} CH_3-\overset{+}{C}H_2 + H_2O$$

All India 2017

36. Write the mechanism of acid dehydration of ethanol to yield ethene. **NCERT**

Or Explain the mechanism of the following reaction:

$$CH_3-CH_2-OH \xrightarrow[443\ K]{H^+} CH_2{=}CH_2 + H_2O$$

All India 2013

37. Write the mechanism of the following reaction:

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

All India 2014

38. Why is the reactivity of all the three classes of alcohols with conc. HCl and $ZnCl_2$ (Lucas reagent) different? **NCERT Exemplar**

39. Give equations of the following reactions.
(i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.
(ii) Bromine in CS_2 with phenol.
(iii) Dilute HNO_3 with phenol.
(iv) Treating phenol with chloroform in the presence of aqueous NaOH. **NCERT**

40. How will you convert the following?
(i) Propan-2-ol to propanone
(ii) Phenol to 2, 4, 6-tribromophenol **Delhi 2013**

41. Explain how does –OH group attached to a carbon of benzene ring activate it towards electrophilic substitution? **NCERT**

42. Explain the following with an example.
(i) Kolbe's reaction
(ii) Reimer-Tiemann reaction
All India 2019, NCERT; NCERT Intext

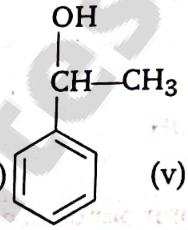
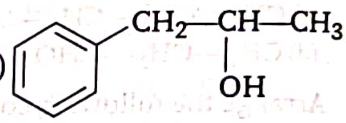
43. Describe the chemical test to distinguish between ethanol and phenol.
All India 2010 C, 2009; Delhi 2008 C

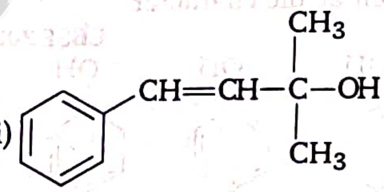
SHORT ANSWER Type II Questions

44. Classify the following as primary, secondary and tertiary alcohols.

(i) $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2OH$ (ii) $H_2C{=}CH-CH_2OH$

(iii) $CH_3-CH_2-CH_2-OH$

(iv)  (v) 

(vi) 

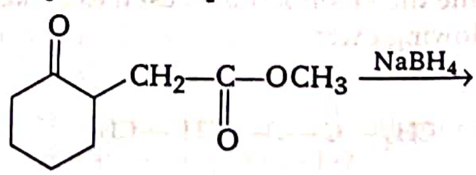
NCERT Intext

45. Give the structures and IUPAC names of monohydric phenols of molecular formula C_7H_8O. **NCERT**

46. Synthesise the following.
(i) Butene to butanol
(ii) 1-chloropropane to propan-1-ol
(iii) Benzoic acid to benzyl alcohol

47. Draw the structure of the products of the following reactions.

(i) $CH_3-CH{=}CH_2 \xrightarrow{H_2O\ /\ H^+}$

(ii) 

(iii) $CH_3CH_2-\underset{CH_3}{\underset{|}{CH}}-CHO \xrightarrow{NaBH_4}$

NCERT Intext

48. Show how will you synthesise
(i) 1-phenyl ethanol from a suitable alkene?
(ii) cyclohexyl methanol using an alkyl halide by an S_N2 mechanism?
(iii) pentan-1-ol using an alkyl halide? **NCERT**

49. Predict the major product of acid catalysed dehydration of
   (i) 1-methyl cyclohexanol
   (ii) butan-1-ol **NCERT Intext**

50. Name the reagent in the following reactions.
   (i) Oxidation of primary alcohol to a carboxylic acid.
   (ii) Oxidation of primary alcohol to an aldehyde.
   (iii) Bromination of phenol to 2,4,6-tribromophenol.
   (iv) Benzyl alcohol to benzoic acid.
   (v) Dehydration of propan-2-ol to propene.
   (vi) Butan-2-one to butan-2-ol. **NCERT**

51. Give the structures of the products you would expect when each of the following alcohol reacts with
   (i) HCl-$ZnCl_2$
   (ii) HBr and
   (iii) $SOCl_2$
      (a) Butan-1-ol
      (b) 2-methylbutan-2-ol

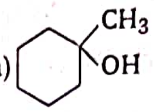
52. How may be the following transformation carried out (in not more than six steps)? Ethyl alcohol to vinyl acetate.

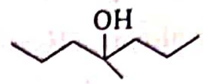
53. Draw the structure and name the product formed if the following alcohols are oxidised. Assume that an excess of oxidising agent is used. **Delhi 2012**
   (i) $CH_3CH_2CH_2CH_2OH$
   (ii) butan-2-ol
   (iii) 2-methyl-propan-1-ol

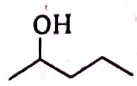
LONG ANSWER Type Questions

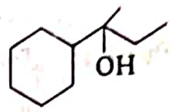
54. (i) Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names.
   (ii) Classify the isomers of alcohols in the above question as primary, secondary and tertiary alcohols. **NCERT**

55. (i) Show how would you synthesise the following alcohols from alkenes?

(a) 

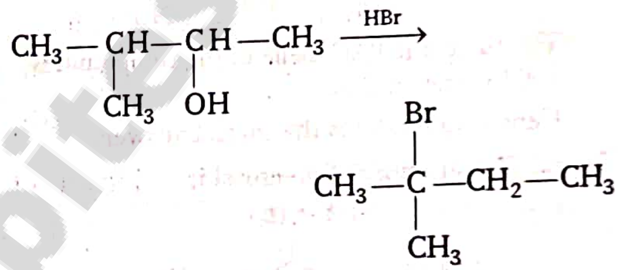
(b) 

(c) 

(d) 

   (ii) While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason. **NCERT**

56. (i) When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:



   Give a mechanism for this reaction.
   (ii) What is meant by hydroboration-oxidation reaction? Illustrate it with an example. **NCERT**

57. (i) How are the following conversions carried out?
      (a) Propene → Propan-2-ol **Delhi 2013**
      (b) Benzyl chloride → Benzyl alcohol **Delhi 2010**
      (c) Ethyl magnesium chloride → Propan-1-ol **Delhi 2010**
      (d) Methyl magnesium bromide → 2-methyl propan-2-ol. **Delhi 2010; NCERT**
   (ii) Explain why propanol has higher boiling point than that of butane? **NCERT**

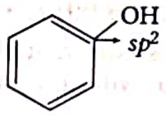
58. (i) Explain with reason:
      (a) Presence of electron withdrawing group increases the acidic character of phenol.
      (b) Solubility of alcohols in water decreases with increase in molecular mass.
      (c) Phenol is more acidic than ethanol.
   (ii) How would you obtain
      (a) picric acid from phenol?
      (b) 2-methyl propanol from 2-methyl propene?

HINTS AND EXPLANATIONS

1. (*a*) Allylic alcohol, $CH_2{=}CH{-}\underset{\underset{sp^3}{\downarrow}}{CH_2OH}$

Vinyl alcohol, $CH_2{=}\underset{\underset{sp^2}{\uparrow}}{CH}{-}OH$

Phenol,



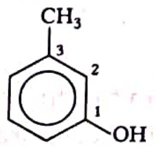
2. (*c*)

$$\overset{6}{CH_3}-\underset{\underset{Cl}{|}}{\overset{5}{CH}}-\overset{4}{CH_2}-\overset{3}{CH_2}-\underset{\underset{OH}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$$

The correct IUPAC name of the compound is 5-chlorohexan-2-ol.

Hence, option (c) is the correct answer.

3. (*a*) The structure of *m*-cresol is



m-cresol

IUPAC name is 3-methylphenol because —OH is the functional group and the methyl is substituent.

4. (*a*) The three isomers of butanol are possible but only one possess chiral centre.

(i) $\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH}$ (ii) $\underset{\text{Butan-2-ol}}{CH_3CH_2-\underset{\underset{OH}{|}}{CH}-CH_3}$

(iii) $\underset{\substack{\text{2-methylpropan-2-ol}\\\text{(chiral)}}}{H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3}$

5. (*c*) An amide on reaction with NaOH and Br_2 in alcoholic medium gives primary amines containing one carbon less than the starting amide. This reaction is called as Hoffman-Bromamide reaction. Complete reaction is as follows:

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + NaOH \xrightarrow[\text{NaOH/KOH}]{\text{Ethanolic solution of}} \underset{\text{Methyl amine}}{CH_3NH_2}$$

6. (*b*) The process of converting alkyl halides into alcohols involves substitution reaction.

$$\underset{\text{Alkyl halide}}{R-X} \xrightarrow{OH^-} \underset{\text{Alcohol}}{R-OH}$$

7. (*b*) In *o*-nitrophenol, nitro group is present at *ortho* position. Presence of electron withdrawing group at *ortho* position increases the acidic strength. On the other hand, in *o*-methylphenol and in *o*-methoxyphenol, electron releasing group ($-CH_3$, $-OCH_3$) are present.

Presence of these groups at *ortho* or *para* positions of phenol decreases the acidic strength of phenols. So, phenol is less acidic than *o* - nitrophenol.

8. (*c*) Ethanal (CH_3CHO) is an oxidised product of ethanol. Pyridinium chlorochromate ($C_6H_5NHClCrO_3$) oxidises primary alcohols to aldehydes. It stops reaction at the aldehydic stage. Strong oxidising agents such as $KMnO_4$ are used for getting carboxylic acid from alcohols.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{\text{PCC}} \underset{\text{Ethanal}}{CH_3CHO}$$

9. (*a*) Alcohols form intermolecular hydrogen bonds, that's why their boiling points are higher.

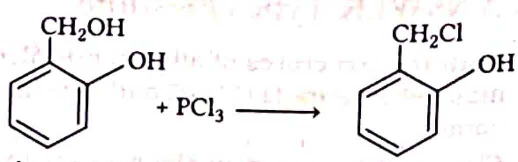
10. (*c*) Lower molecular mass alcohols are able to form hydrogen bonds with water. Thus, are miscible in all proportions.

11. (*b*) Phenol does not undergo nucleophilic substitution reaction easily due to partial double bond character of C—OH bond.

12. (*d*) $\underset{\text{2-methyl propanal}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{H}{|}}{C}{=}O} + \underset{\substack{\textit{Iso}\text{-propyl magnesium}\\\text{iodide}}}{(CH_3)_2CHMgI} \longrightarrow$

$$(CH_3)_2CH-\underset{\underset{CH(CH_3)_2}{|}}{\overset{\overset{H}{|}}{C}}-OMgI \xrightarrow{H_2O} \underset{\text{2, 4-dimethyl pentan-3-ol}}{(CH_3)_2CH-\underset{\underset{CH(CH_3)_2}{|}}{\overset{\overset{H}{|}}{C}}-OH}$$

13. (*b*)



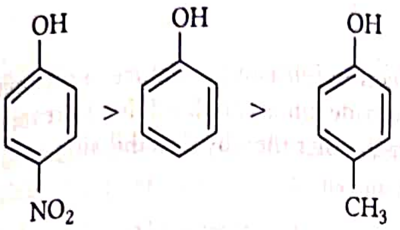
o-hydroxy benzyl alcohol → 2-chloromethyl phenol

14. (*b*) NaCl will not convert ethyl alcohol into ethyl chloride.

15. (*b*) With conc. HNO_3, phenol is converted to 2, 4, 6-trinitrophenol.

16. (*c*) $\underset{\substack{(X)\\\text{Propanol}}}{CH_3CH_2CH_2-OH} \xrightarrow{\text{On oxidation}} \underset{\substack{(Y)\\\text{Propanoic acid}}}{CH_3CH_2COOH}$

17. (*b*) Electron releasing group decreases while electron withdrawing group increases acidic strength by destabilising and stabilising the phenoxide ion formed respectively.



(II) (III) (I)

($-M, -I$) ($+I$, hyperconjugation)

18. $\overset{4}{H_3C}-\underset{CH_3}{\overset{3}{C}}=\underset{Br}{\overset{2}{C}}-\overset{1}{CH_2}-OH$

2-bromo-3-methyl-but-2-en-1-ol

19. $CH_3-\overset{OH}{CH}-CH_3$

Propan-2-ol

20. R must be a group having more electron density than H, i.e. having $+I$-effect whereas R' must be having $-I$- effect.

21. The correct order of dehydration of alcohols is: Tertiary alcohols > Secondary alcohols > Primary alcohols

22. In phenols, the lone pairs of electrons on the oxygen atom are delocalised over the benzene ring due to resonance and hence, are not easily available for protonation to destabilise O—H bond thus, making protonation difficult.

23. The complex of CrO_3, pyridine and HCl, i.e. PCC (pyridinium chlorochromate), oxidises $\rangle$CHOH to $\rangle C=O$ without carrying out oxidation of double bond.

24. Refer to text on page 272.

25. Refer to text on page 267.

26. **Hint** In phenol, C—O bond is less polar due to electron withdrawing effect of the benzene ring whereas in methanol, C—O bond is more polar due to electron releasing effect of $-CH_3$ group.

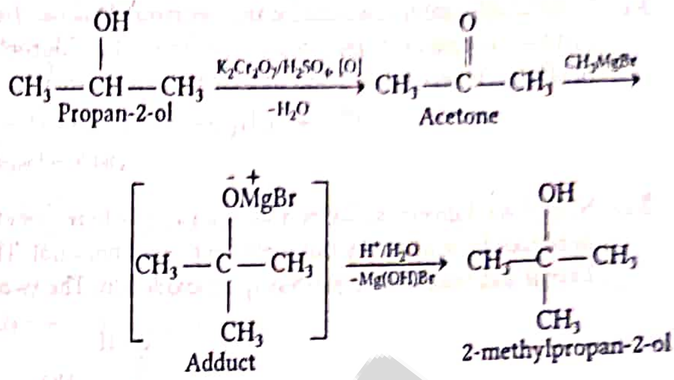
27. (i) Propene to propan-1-ol

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{\text{Propyl bromide}}{CH_3CH_2CH_2Br}$$

$$\xrightarrow{Aq.\ KOH} \underset{\text{Propan-1-ol}}{\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH}$$

(ii) Refer to text on page 266.

28. (i) Propan-2-ol to 2-methylpropan-2-ol

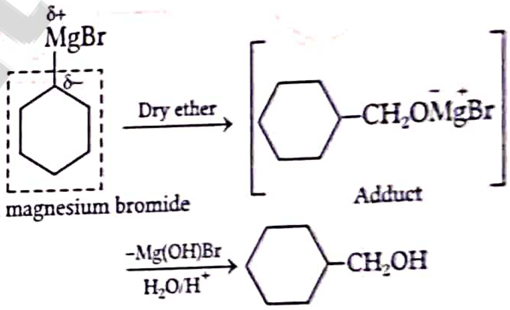


(ii) Refer to text on page 266.

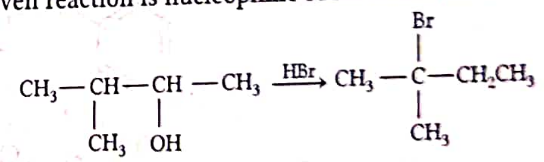
29. (i) $\underset{\text{Methanal}}{HCHO} + (CH_3)_2CH\overset{\delta-}{}\overset{\delta+}{MgBr} \xrightarrow{\text{Dry ether}}$

$$\underset{\text{Adduct}}{[(CH_3)_2CHCH_2\overset{-}{O}\overset{+}{M}gBr]} \xrightarrow[-Mg(OH)Br]{H_2O/H^+} \underset{\text{2-methylpropan-1-ol}}{(CH_3)_2CH-CH_2OH}$$

(ii) HCHO +

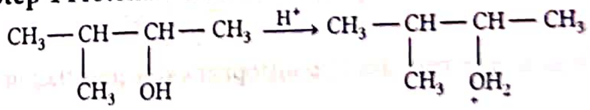


30. Given reaction is nucleophilic substitution reaction.

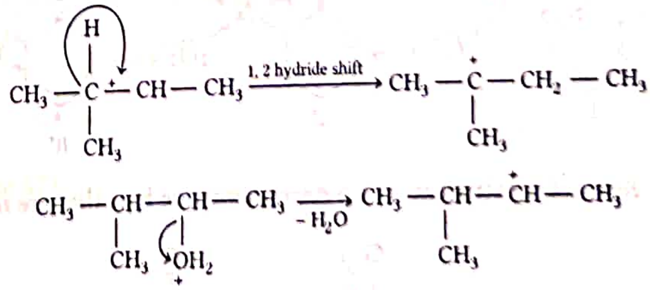


Mechanism

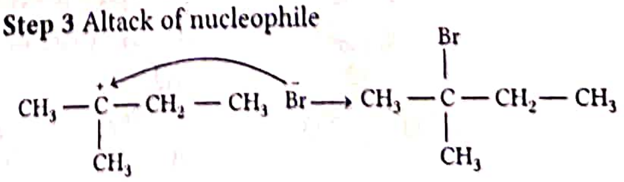
Step 1 Protonation of alcohol



Step 2 Formation of carbocation



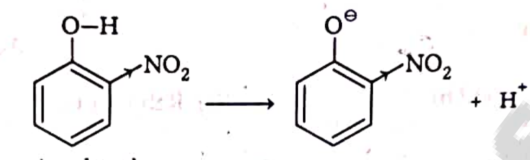
Step 3 Attack of nucleophile



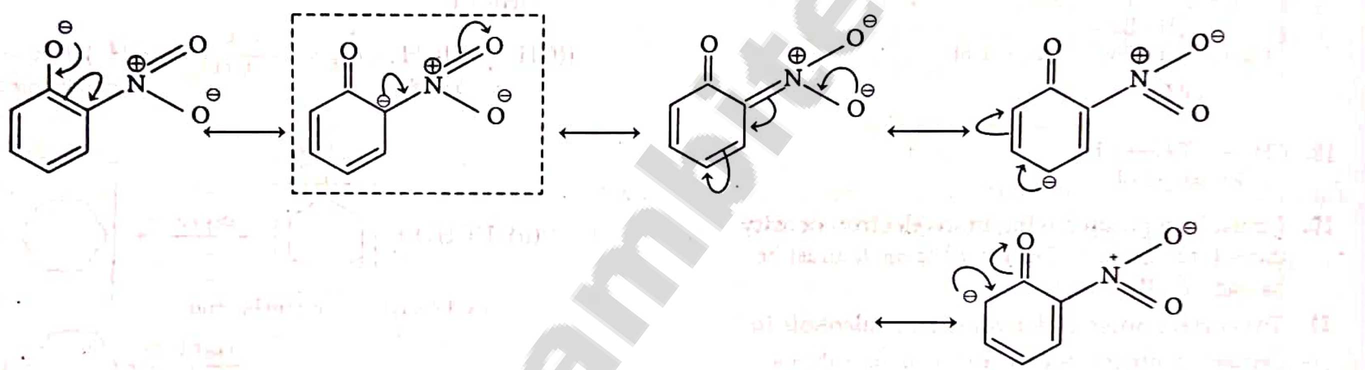
31. 2-chloroethanol is more acidic than ethanol. Due to $-I$-effect (electron withdrawing group) of the Cl-atom, electron density on O—H bond decreases. So, O—H bond of 2-chloroethanol becomes weaker than O—H bond of ethanol. Thus, the release of H^+ ion from O — H bond of 2-chloroethane becomes easier.

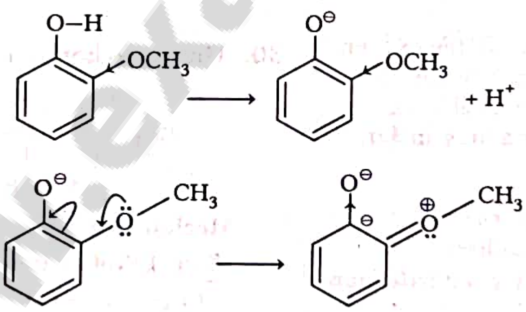
$$\underbrace{Cl \leftarrow CH_2 \leftarrow CH_2 \leftarrow O \leftarrow H}_{\text{OH bond weakens}} > CH_3 \rightarrow CH_2 \rightarrow O \rightarrow H$$

32. Nitro (NO_2) group is electron withdrawing whereas methoxy (OCH_3) group is electron releasing in nature. o-nitrophenol produces H^+ ions easily but methoxyphenol does not. This is because o-nitrophenoxide ion is stabilised due to resonance. This is not true with o-methoxyphenoxide ion. The two negative charges repel each other thereby destabilising it.

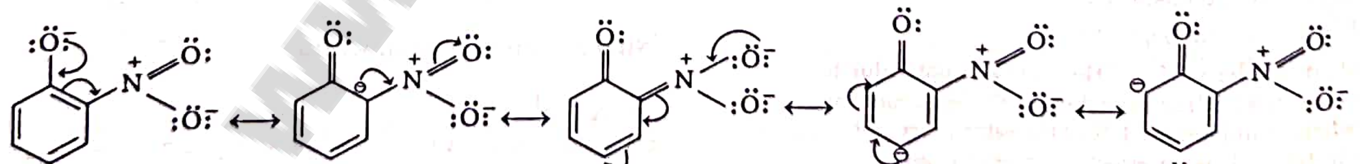


o-nitrophenol



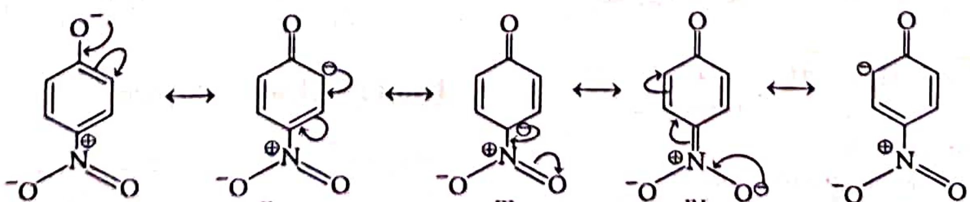


33. Resonating structures of o-nitrophenoxide ions that are formed by the loss of proton from o-nitrophenol are as follows:



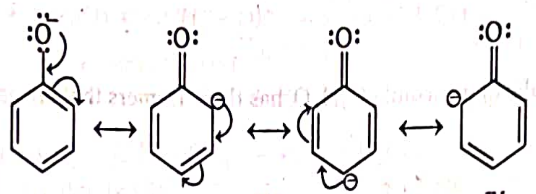
I II III IV V

Resonating structures of p-nitrophenoxide ions that are formed by the loss of proton from p-nitrophenol are as follows:



I II III IV V

Resonating structures of phenoxide ions that are formed by the loss of proton from phenol are as follows:

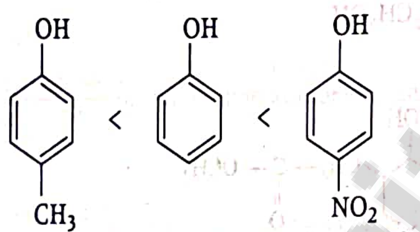


I II III IV

It is clearly evident from the above structures that due to $-R$-effect of — NO_2 group, *o*-and *p*-nitrophenoxide ions are more stable than phenoxide ions. Consequently, *o*- and *p*-nitrophenols are more acidic than phenols.

34. (i) Refer to text on page 268.
(ii) Refer to text on page 264.

35. (i) Electron withdrawing groups such as — NO_2, increases the acidic character while electron releasing group such as — CH_3 decreases the acidic character thus, the increasing order of acidic strength is



(*p*-cresol) (Phenol) (*p*-nitrophenol)

(ii) The mechanism for the formation of carbocation is as follows

$$CH_2{=}CH_2 + H{-}\overset{\overset{\Large H}{|}}{\overset{+}{\ddot{O}}}{-}H \longrightarrow CH_3{-}\overset{+}{C}H_2 + H_2O$$

36. Refer to mechanism of dehydration of alcohols on page 270.

37. The mechanism of the given reaction can be predicted as:

Step 1. $HBr \longrightarrow H^+ + Br^-$

Step 2. $CH_3{-}CH_2{-}\ddot{O}H + H^+ \longrightarrow CH_3{-}CH_2{-}\overset{+}{O}H_2 \xrightarrow[S_N2\ \text{reaction}]{Br^-} CH_3{-}CH_2{-}Br + H_2\ddot{O}$

38. The reaction of alcohols with Lucas reagent (conc. HCl and $ZnCl_2$) follows S_N1 mechanism which depends upon the stability of carbocations (intermediate). More stable the intermediate carbocation, more reactive is the alcohol.
Tertiary carbocations are most stable among the three classes of carbocations and the order of the stability of carbocation is $3° > 2° > 1°$. This order, in turn, reflects the order of reactivity of three classes of alcohols, i.e. $3° > 2° > 1°$.
Thus, as the stability of carbocations are different so the reactivity of all the three classes of alcohols with Lucas reagent is different.

39. (i) $\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + 2[O] \xrightarrow[\text{Oxidation}]{\text{Alk. }KMnO_4} CH_3CH_2CO\bar{O}K^+ \xrightarrow[\text{Acidification}]{H^+/H_2O} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$

(ii) Refer to halogenation on page 272.
(iii) Refer to nitration on page 271.
(iv) Refer to Reimer-Tiemann reaction on page 272.

40. (i) Refer to text on page 271. (ii) Refer to text on page 272.

41. Refer to text on page 271.

42. Refer to text on page 272.

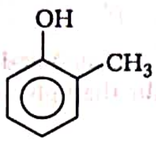
43. Ethanol when warmed with NaOH+ I_2, gives yellow ppt. of iodoform while phenol does not give this test.

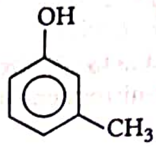
$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 4NaOI \longrightarrow \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3\downarrow} + HCOO^-Na^+ + NaI + H_2O + 2NaOH$$

$$\underset{\text{Phenol}}{C_6H_5OH} + NaOH \longrightarrow \text{No yellow ppt.}$$

44. Primary alcohols-(i), (ii), (iii)
Secondary alcohols-(iv), (v)
Tertiary alcohols-(vi)

45. The phenolic compound with molecular formula C_7H_8O, has three isomers that are as follows:


o-cresol or 2-methylphenol


m-cresol or 3-methylphenol


p-cresol or 4-methylphenol

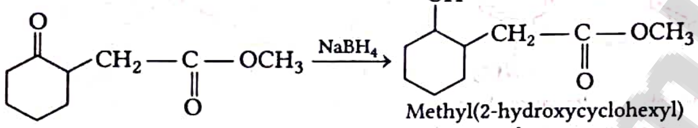
46. (i) Refer to text on page 264.

(ii) $CH_3CH_2CH_2Cl \xrightarrow{Aq.\ NaOH} CH_3CH_2CH_2OH$

(iii) Refer to text on page 265.

47. (i) Refer to text on page 264.

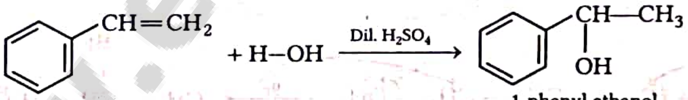
(ii)


Methyl(2-hydroxycyclohexyl) ethanoate

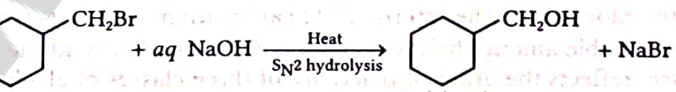
(iii) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CHO \xrightarrow{NaBH_4} CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$

2-methylbutan-1-ol

48. (i) On adding H_2O to ethenyl benzene in the presence of dil. H_2SO_4, we get 1-phenyl ethanol.


Ethenyl benzene　　1-phenyl ethanol

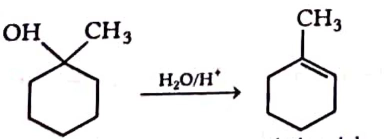
(ii) Hydrolysis of cyclohexyl methyl bromide by aqueous NaOH gives cyclohexyl methanol.


Cyclohexyl methyl bromide　　Cyclohexyl methanol

(iii) Hydrolysis of 1-bromopentane by aqueous NaOH, gives pentan-1-ol.

$$\underset{\text{1-bromopentane}}{CH_3CH_2CH_2CH_2CH_2-Br} + NaOH \xrightarrow[S_N2\ \text{hydrolysis}]{\text{Heat}} \underset{\text{Pentan-1-ol}}{CH_3CH_2CH_2CH_2CH_2-OH} + NaBr$$

49. (i)


1-methyl cyclohexanol　　1-methyl cyclohex 1-ene

(ii) $\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2-\ddot{O}H} \xrightarrow{+H^+} \underset{\text{Protonated alcohol}}{CH_3CH_2CH_2CH_2-\overset{+}{\ddot{O}}H_2} \xrightarrow{-H_2O} \underset{\text{1° carbocation}}{CH_3CH_2-\underset{H}{\underset{|}{C}}H-\overset{+}{C}H_2}$

$\xrightarrow{\text{1, 2-hydride shift}} \underset{\substack{\text{2° carbocation (II)} \\ \text{(More stable)}}}{CH_3-CH_2-\overset{\oplus}{C}H-CH_3} \xrightarrow[-H^+]{} \underset{\substack{\text{But-1-ene} \\ \text{(Minor)}}}{CH_3CH_2CH=CH_2} + \underset{\substack{\text{But-2-ene} \\ \text{(Major)}}}{CH_3-CH=CH-CH_3}$

50. (i) Acidified $K_2Cr_2O_7$ (followed by hydrolysis with dil. H_2SO_4)
(ii) Pyridinium chlorochromate (PCC)
(iii) Aqueous bromine
(iv) Acidified or alkaline $KMnO_4$ (followed by hydrolysis with dil. H_2SO_4)
(v) 85% H_3PO_4 at 440 K
(vi) Ni/H_2 or $NaBH_4$ or $LiAlH_4$

51. (i) **With HCl-$ZnCl_2$** (Lucas reagent)

(a) $\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2-OH} + \underset{\text{(Conc.)}}{HCl} \xrightarrow{\text{Anhy. }ZnCl_2}$ No reaction at room temperature

(b) $\underset{\text{2-methylbutan-2-ol}}{CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2CH_3} + HCl \xrightarrow{\text{Anhy. }ZnCl_2} \underset{\substack{\text{2-chloro-2-methylbutane} \\ \text{(White turbidity)}}}{CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_2CH_3} + H_2O$

(ii) **With HBr**

(a) $\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} + HBr \xrightarrow{\text{Heat}} \underset{\text{1-bromobutane}}{CH_3CH_2CH_2CH_2Br} + H_2O$

(b) $\underset{\text{2-methylbutan-2-ol}}{CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2CH_3} + HBr \xrightarrow{\text{Heat}} \underset{\text{2-bromo-2-methylbutane}}{CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_2CH_3} + H_2O$

(iii) **With $SOCl_2$**

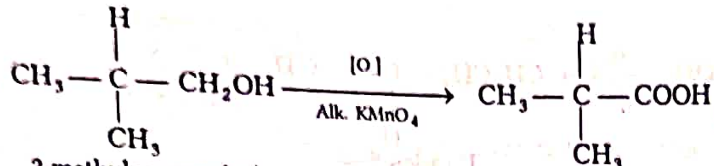
(a) $\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} + SOCl_2 \xrightarrow{\text{Heat}} \underset{\text{1-chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + SO_2\uparrow + HCl$

(b) $\underset{\text{2-methylbutan-2-ol}}{CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2CH_3} + SOCl_2 \xrightarrow{\text{Heat}} \underset{\text{2-chloro-2-methylbutane}}{CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_2CH_3} + SO_2\uparrow + HCl$

52. $\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[\Delta]{\text{Conc. }H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow{NaNH_2} Na-C\equiv C-H \xrightarrow[CH_3COOH]{Hg(CH_3COO)_2} \underset{\text{Vinyl acetate}}{CH_2=CH-OCOCH_3}$

53. (i) $\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\substack{\text{Oxidation} \\ KMnO_4\text{(alk.)}}]{[O]} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$

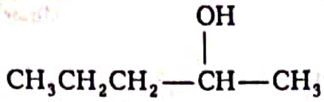
(ii) $\underset{\text{Butan-2-ol}}{CH_3-\underset{OH}{\underset{|}{C}}H-CH_2CH_3} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} \underset{\text{Butan-2-one}}{CH_3-\underset{O}{\underset{\|}{C}}-CH_2CH_3}$

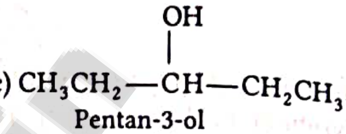
(iii) 

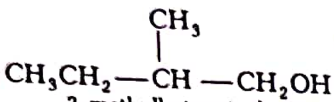
2-methylpropan-1-ol → 2-methylpropanoic acid

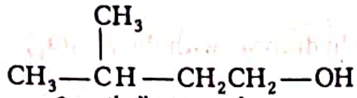
54. (i) Eight isomers are possible.

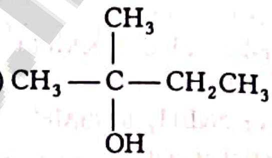
(a) $CH_3CH_2CH_2CH_2CH_2OH$
Pentan-1-ol

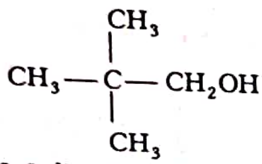
(b) 
Pentan-2-ol

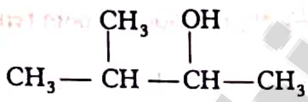
(c) 
Pentan-3-ol

(d) 
2-methylbutan-1-ol

(e) 
3-methylbutan-1-ol

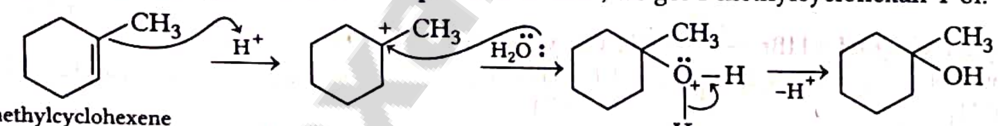
(f) 
2-methylbutan-2-ol

(g) 
2, 2-dimethyl propan-1-ol

(h) 
3-methylbutan-2-ol

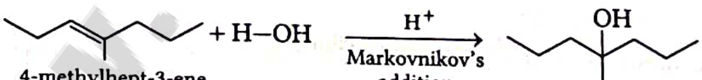
(ii) In the above isomers,
Primary alcohols – (a), (d), (e), (g); Secondary alcohols – (b), (c), (h); Tertiary alcohols – (f)

55. (i) (a) On adding H_2O to 1-methylcyclohexene in the presence of acid, we get 1-methylcyclohexan-1-ol.



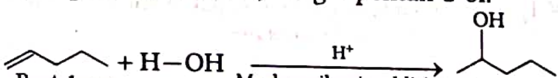
1-methylcyclohexene → 1-methylcyclohexan-1-ol

(b) When we add H_2O to 4-methylhept-3-ene in the presence of an acid, we get 4-methylheptan-4-ol.



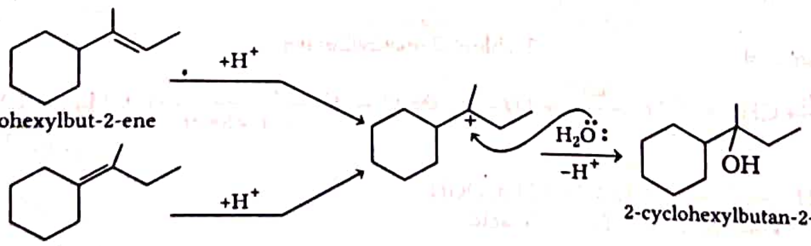
4-methylhept-3-ene → 4-methylheptan-4-ol

(c) On adding H_2O to pent-1-ene in presence of acid, we get pentan-2-ol.



Pent-1-ene → Pentan-2-ol

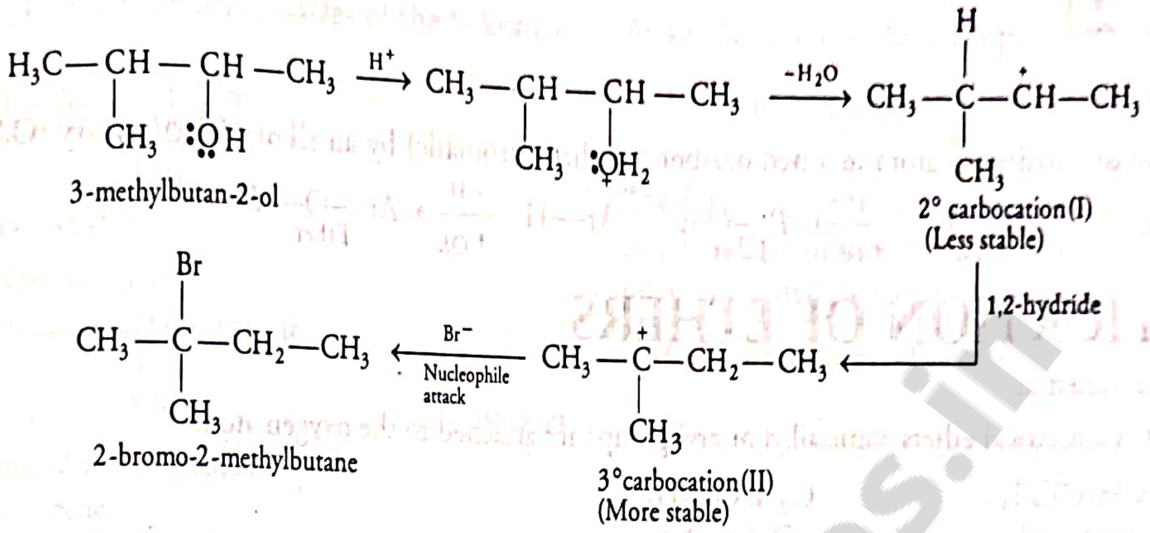
(d) When we add H_2O to 2-cyclohexylbut-2-ene or 2-cyclohexylidenebutane, in the presence of an acid, in both the cases the product is same, i.e. 2-cyclohexylbutan-2-ol.



2-cyclohexylbut-2-ene; 2-cyclohexylidenebutane → 2-cyclohexylbutan-2-ol

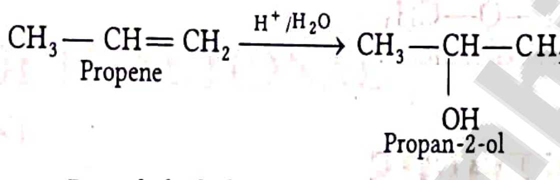
(ii) *o*-nitrophenol is steam volatile due to intramolecular H-bonding and hence, can be separated by steam distillation from *p*-nitrophenol, which is not steam volatile.
[For structures, refer to text on page 269.]

56. (i) We get a 2° carbocation by the protonation of 3-methylbutan-2-ol followed by the loss of H_2O. It is rearranged by 1, 2-hydride shift to more stable 3° carbocation (II). Nucleophilic attack by Br^- ion on this carbocation (II) gives the final product.

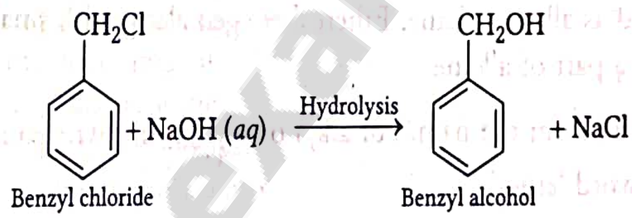


(ii) Refer to text on page 265.

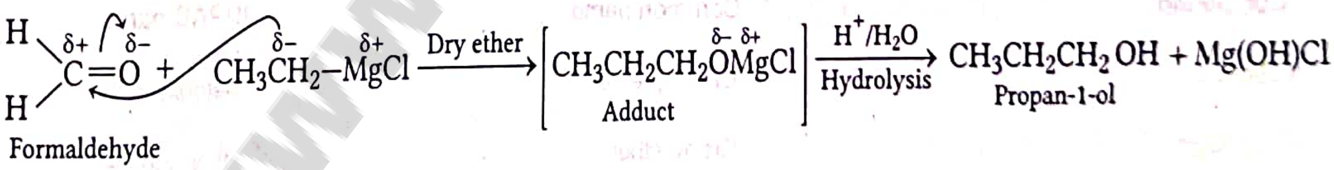
57. (i) (a) Propene ⟶ Propan-2-ol



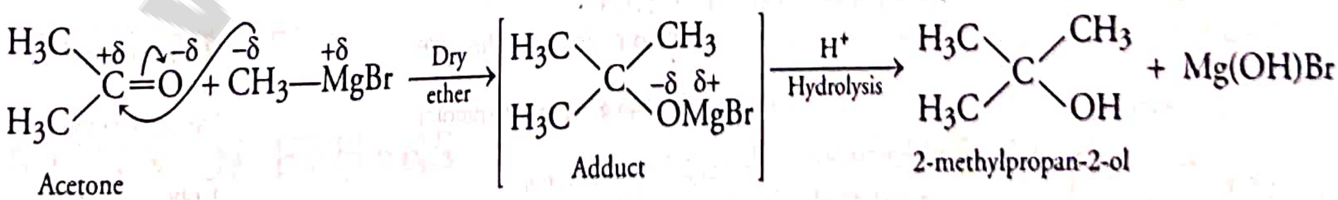
(b) Benzyl chloride ⟶ Benzyl alcohol



(c) Ethyl magnesium chloride ⟶ Propan-1-ol



(d) Methyl magnesium bromide ⟶ 2-methylpropan-2-ol



(ii) Refer to text on page 267.

58. (i) (a) Refer to text on page 269.

(b) Refer to text on page 267.

(c) Refer to text on page 268.

(ii) (a) Refer to text on page 272.

(b) Refer to text on pages 264 and 265.

|TOPIC 2|
Ethers

The substitution of a hydrogen atom in a hydrocarbon (aliphatic/aromatic) by an alkoxy (O*R*)/aryloxy (OAr) group yield ethers. e.g.

$$\underset{\text{Alkane}}{R\text{—H}} \xrightarrow[+OR]{-H} \underset{\text{Ether}}{R\text{—O}R}; \qquad \text{Ar—H} \xrightarrow[+OR]{-H} \underset{\text{Ether}}{\text{Ar—O—}R}$$

CLASSIFICATION OF ETHERS

Ethers can be classified as

(i) **Simple or symmetrical ethers** Same alkyl or aryl groups are attached to the oxygen atom.

e.g. $\underset{\text{Dimethyl ether}}{CH_3OCH_3}$, $\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5}$

(ii) **Unsymmetrical ethers** Different alkyl or aryl groups are attached to the oxygen atom.

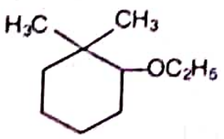
e.g. $\underset{\text{Methyl phenyl ether}}{C_6H_5\text{—O—}CH_3}$, $\underset{\text{Methyl ethyl ether}}{C_2H_5\text{—O—}CH_3}$

NOMENCLATURE OF ETHERS

In IUPAC system, ethers are named as alkoxy alkane. Ethereal oxygen along with smaller alkyl group is called alkoxy. Larger alkyl group is considered as a part of alkane.

Common names of ethers are derived from the names of alkyl or aryl groups written as a separate word in an alphabetical order and adding the word 'ether'.

Common and IUPAC names of some ethers

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OCH_2CH_2CH_3$	Methyl *n*-propyl ether	1-methoxypropane
$C_6H_5OCH_3$	Methyl *n*-phenyl ether (anisole)	Methoxybenzene
$C_6H_5OCH_2CH_3$	Ethyl phenyl ether (phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6\text{—}CH_3$	Heptyl phenyl ether	1-phenoxyheptane
$CH_3O\text{—}CH(CH_3)\text{—}CH_3$	Methyl *iso*-propyl ether	2-methoxypropane
$C_6H_5\text{—O—}CH_2\text{—}CH_2\text{—}CH(CH_3)\text{—}CH_3$	Phenyl *iso*-pentyl ether	3-methylbutoxybenzene
$CH_3\text{—O—}CH_2\text{—}CH_2\text{—}OCH_3$	—	1, 2-dimethoxyethane
	—	2-ethoxy-1,1-dimethylcyclohexane

EXAMPLE |1| Write the IUPAC names of the following compounds.

$$CH_3-O-CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_3$$

$$C_6H_5-O-C_2H_5$$

$$C_6H_5-O-C_7H_{15}(n\text{-})$$

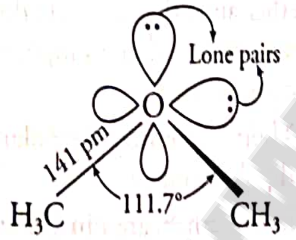
$$CH_3-CH_2-O-\underset{\substack{|\\CH_3}}{CH}-CH_2CH_3$$

NCERT

Sol. (i) 1-methoxy-2-methylpropane
(ii) Ethoxybenzene
(iii) 1-phenoxyheptane
(iv) 2-ethoxybutane

STRUCTURE OF FUNCTIONAL GROUP (ETHERS)

In ethers, the four electron pairs, i.e. the two bond pairs and two lone pairs of electrons on oxygen are arranged in approximate tetrahedral arrangement. Bond angle is slightly greater than tetrahedral angle because of the repulsive interaction between two bulky (*—R*) groups. The C—O bond length (141 pm) is almost the same as in alcohols. e.g., methoxy methane.



Structure of methoxy methane

PREPARATION OF ETHERS

Ethers can be prepared by the following methods :

By the Dehydration of Alcohols

Alcohols undergo dehydration in the presence of protic acids such as H_2SO_4, H_3PO_4. Formation of the reaction product, alkene or ether depends upon the reaction conditions, e.g. ethanol is dehydrated to ethoxyethane at 413 K in the presence of sulphuric acid.

$$\underset{\substack{\text{Ethanol}\\\text{(Excess)}}}{2C_2H_5OH} \xrightarrow[413\text{ K}]{\text{Conc. }H_2SO_4} \underset{\text{Ethoxyethane}}{C_2H_5-O-C_2H_5} + H_2O$$

At 443 K, ethene is the main product.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[443\text{ K}]{H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$$

The formation of ether is a nucleophilic bimolecular reaction, S_N2. It involves the attack of alcohol molecule on a protonated alcohol as shown below :

Step I Protonation of alcohol

$$CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H + H^+ \xrightarrow{\text{Fast}} CH_3-CH_2-\overset{+}{\underset{\cdot\cdot}{O}}(H)-H$$

Step II Nucleophilic attack by unprotonated alcohol molecule on protonated alcohol molecule.

$$CH_3CH_2-\underset{\substack{|\\H}}{\ddot{O}}: + CH_3-CH_2-\overset{+}{O}\langle^{H}_{H} \xrightarrow[\text{Slow}]{S_N2} \underset{\text{Protonated ethoxy ethane}}{CH_3CH_2-\underset{\substack{|\\H}}{\overset{+}{O}}-CH_2CH_3} + H_2O$$

Step III Loss of proton to form ethoxy ethane

$$CH_3CH_2-\underset{\substack{|\\H}}{\overset{+}{O}}-CH_2CH_3 \xrightarrow{\text{Fast}} \underset{\text{Ethoxy ethane}}{CH_3CH_2-O-CH_2CH_3} + H^+$$

Note Acidic dehydration of alcohols to give an alkene is also associated with substitution reaction to give an ether.

Limitations

This method is not suitable for the preparation of unsymmetrical ethers since, complex mixture is obtained. This method is suitable for the preparation of ethers having primary alkyl groups only. The alkyl group should be unhindered and the temperature should be kept low otherwise alkene is formed. In case of 2° and 3° alcohols, the reaction follow S_N1 pathway and the main product is alkene because elimination competes over substitution. The order of dehydration of alcohols leading to the formation of ethers follows the order 1° > 2° > 3° alcohols.

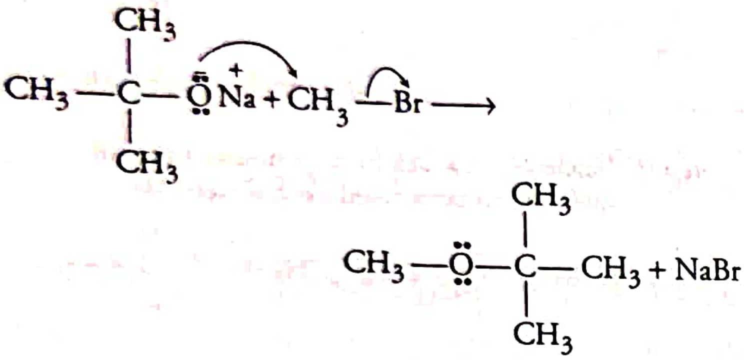
Williamson's Synthesis

This is one of the best and important laboratory methods for the preparation of symmetrical and

unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.

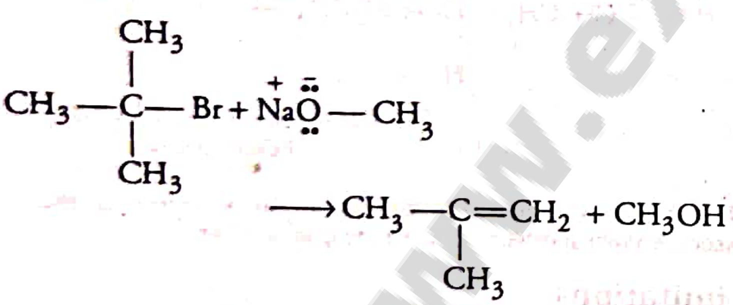
$$\underset{\text{Alkyl halide}}{R—X} + \underset{\text{Sodium alkoxide}}{R'—\ddot{\underset{..}{O}}\overset{+}{N}a} \longrightarrow \underset{\text{Ether}}{R—\ddot{\underset{..}{O}}—R'} + \underset{\text{Sodium halide}}{NaX}$$

Ethers containing substituted alkyl groups (secondary or tertiary) may be prepared by this method. This reaction involves S_N2 attack of an alkoxide ion on primary alkyl halide. Better results are obtained, if the alkyl halide is primary.



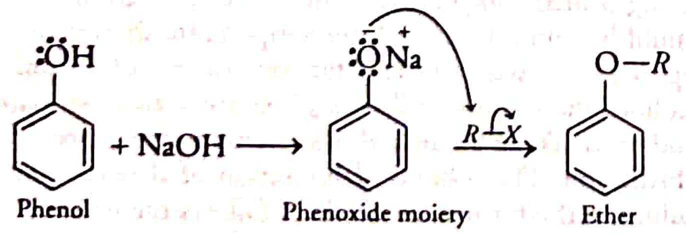
2-methoxy-2-methyl propane

In case of 2° and 3° alkyl halides, due to steric hindrance, elimination competes over substitution and alkenes are formed. It is because alkoxides are not only nucleophiles but strong bases as well. These react with alkyl halides leading to the elimination reaction.



2-methylpropene

Phenols are also converted to ethers by this method. In this method, phenol is used as the phenoxide moiety.

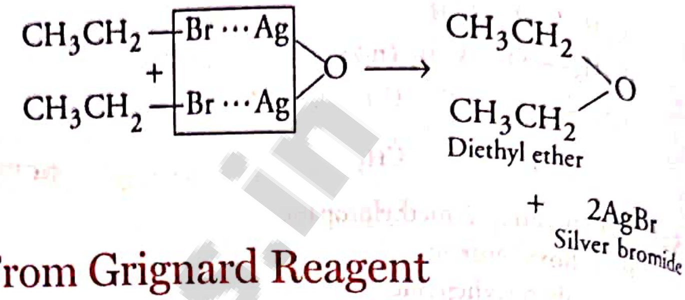


Note

For the synthesis of unsymmetrical ethers, a proper choice of reactants is necessary. This method cannot be used for preparing diaryl ethers. It is also not applicable for tertiary alkyl halide as they yield alkene instead of ethers.

Reaction of Alkyl Halides with Dry Silver Oxide

When alkyl halide is heated with silver oxide, symmetrical ether is formed.



From Grignard Reagent

Higher ethers can be prepared by treating α-haloethers with suitable Grignard reagent.

$$\underset{\text{Chloromethoxy methane}}{CH_3—O—CH_2Cl} + CH_3MgI \xrightarrow{\text{Dry ether}} \underset{\text{Ethyl methyl ether}}{CH_3—OCH_2CH_3} + \underset{\text{Chloro magnesium iodide}}{Mg(Cl)I}$$

PHYSICAL PROPERTIES

Some of the important physical properties of ethers are as follows:

(i) Dimethyl ether and ethyl methyl ethers are gases at ordinary temperature whereas higher ones are liquids with characteristic smell.

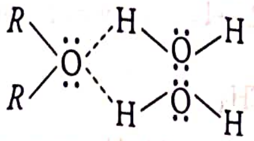
(ii) The C—O bonds in ethers are polar, therefore ethers have a net dipole moment.

(iii) Boiling points of ethers are much lower than the boiling points of alcohols. The large difference in boiling points of alcohols and ethers is due to the presence of H-bonding in alcohols. The boiling points of ethers are comparable to alkanes of comparable molecular masses due to their low polarity.

Formula	Nomenclature	Bp/K
$CH_3(CH_2)_3CH_3$	*n*-pentane	309.1
$C_2H_5—O—C_2H_5$	Ethoxy ethane	307.6
$CH_3(CH_2)_3—OH$	Butan -1-ol	390

(iv) Lower ethers (upto three carbon atoms) are soluble in water and their miscibility with water resembles those of alcohols of the same molecular mass. Both ethoxy ethane and butan-1-ol are miscible to almost the same extent, i.e. 7.5 and 9 g per 100 mL H_2O, respectively while pentane is essentially immiscible with H_2O.

This is due to the fact that just like alcohols, oxygen of ether can also form H-bonds with water molecule.



CHEMICAL REACTIONS

Some of the important chemical reactions of ethers are as follows:

Cleavage of C—O Bond in Ethers

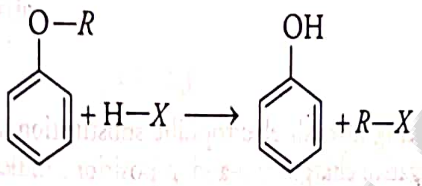
Ethers are least reactive among all functional groups. The cleavage of C—O bond in ethers takes place under drastic conditions with excess of hydrogen halides, *HX*.

The reaction of dialkyl ether gives two alkyl halide molecules.

$$\underset{\text{Ether}}{R\text{—O—}R} + HX \xrightarrow{373\text{ K}} \underset{\text{Alcohol}}{ROH} + \underset{\text{Alkyl halide}}{RX}$$

$$R\text{—OH} + HX \longrightarrow R\text{—}X + H_2O$$

Alkyl aryl ethers are cleaved at alkyl-oxygen bond due to the more stable aryl oxygen bond. The reaction gives phenol and alkyl halide.



The order of reactivity of hydrogen halides is HI > HBr > HCl.

The cleavage of ethers takes place with conc. HI or HBr at high temperature.

Mechanism

Reaction of an ether with conc. HI starts with protonation of ether molecule.

Step I Protonation of ether to form oxonium ion

$$CH_3\text{—}\ddot{O}\text{—}CH_2CH_3 + H\text{—}I \rightleftharpoons \underset{\text{Oxonium ion}}{CH_3\text{—}\overset{H}{\overset{|}{\overset{+}{O}}}\text{—}CH_2CH_3} + I^-$$

The reaction takes place with HI or HBr as these reagents are sufficiently acidic and Br^-/I^- are good nucleophiles.

Step II Iodide being a good nucleophile attacks the least substituted carbon of the oxonium ion formed in step I and it displaces an alcohol molecule by S_N2 mechanism. Therefore, in the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When 1° and 2° alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (S_N2 reaction).

$$I^- + CH_3\text{—}\overset{H}{\overset{|}{\overset{+}{O}}}\text{—}CH_2CH_3 \xrightarrow[\text{Slow}]{S_N2} \left[I\cdots CH_3 \cdots \overset{H}{\overset{|}{\overset{+}{O}}}\text{—}CH_2CH_3 \right]_n \longrightarrow CH_3\text{—}I + CH_3CH_2\text{—}OH$$

Step III If HI is in excess and the reaction is carried out at high temperature, ethanol reacts with another molecule of HI and is converted to ethyl iodide.

$$CH_3CH_2\text{—}\ddot{O}\text{—}H + H\text{—}I \rightleftharpoons CH_3CH_2\text{—}\overset{H}{\overset{|}{\overset{+}{O}}}H + I^-$$

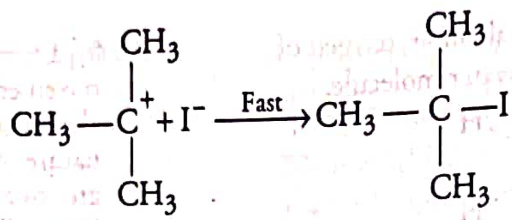
$$I^- + \overset{CH_3}{\overset{|}{C}H_2}\text{—}\overset{+}{O}H_2 \longrightarrow CH_3CH_2I + H_2O$$

If one group is primary alkyl halide, (e.g. methyl group) and other group is tertiary alkyl group, in an ether then (like methanol) primary alkyl group converts into alcohol as a major product and *tert*-alkyl halide is obtained.

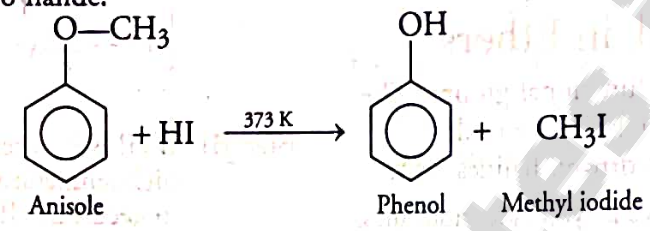
$$\underset{tert\text{-butyl methyl ether}}{CH_3\text{—}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}\text{—}OCH_3} + HI \xrightarrow{373\text{ K}} \underset{tert\text{-butyl iodide}}{CH_3\text{—}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}\text{—}I} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

This reaction follows S_N1 mechanism. This is due to the formation of a more stable carbocation, $(CH_3)_3C^+$ with the departure of leaving group, $CH_3\text{—}OH$.

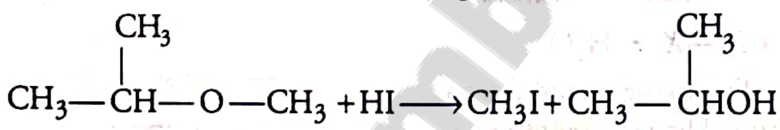
$$CH_3\text{—}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}\text{—}\underset{H}{\overset{+}{O}}\text{—}CH_3 \xrightarrow{\text{Slow}} CH_3\text{—}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C^+}}}} + CH_3OH$$



In case of alkyl aryl ethers such as in anisole, methyl phenyl oxonium ion is formed by the protonation of ether. The bond between O—CH_3 is weaker than the bond between O—C_6H_5 because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character. Thus, the reaction yields phenol and alkyl halide. Phenol does not react further to give halides because sp^2 hybridised carbon of phenol cannot undergo nucleophilic substitution reaction required for conversion to halide.



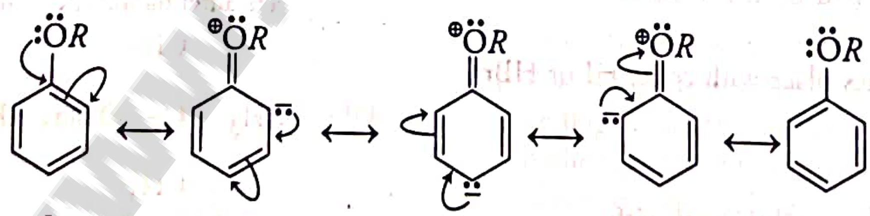
Ethers with two different alkyl groups are also cleaved in the same manner. If primary and secondary alkyl groups are present, the alkyl halide is always formed from the smaller alkyl group.



In benzyl alkyl ethers, cleavage of C—O bond gives alkyl alcohol and benzyl halide through S_N1 mechanism because benzyl carbocation is more stable towards S_N1 mechanism.

Electrophilic Substitution Reaction

Alkoxy group (—O*R*) is *ortho, para* directing and activates the aromatic ring towards electrophilic substitution and directs the incoming electrophile at *o*-and *p*-positions (because of the negative charges at *o*-and *p*-positions indicate the more electron density at these positions).

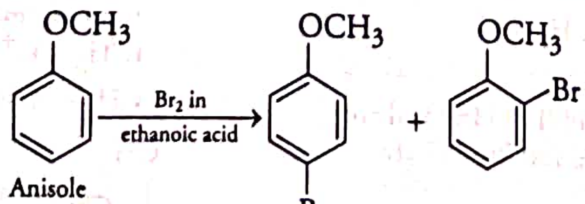


I II III IV V

Important electrophilic substitution reactions are as follows:

(a) Halogenation

Phenylalkyl ethers undergo usual halogenation in the benzene ring, e.g. anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by the methoxy group. Halide group is introduced at *o*-and *p*-positions of the ring. *p*-isomer is obtained in 90% yield.

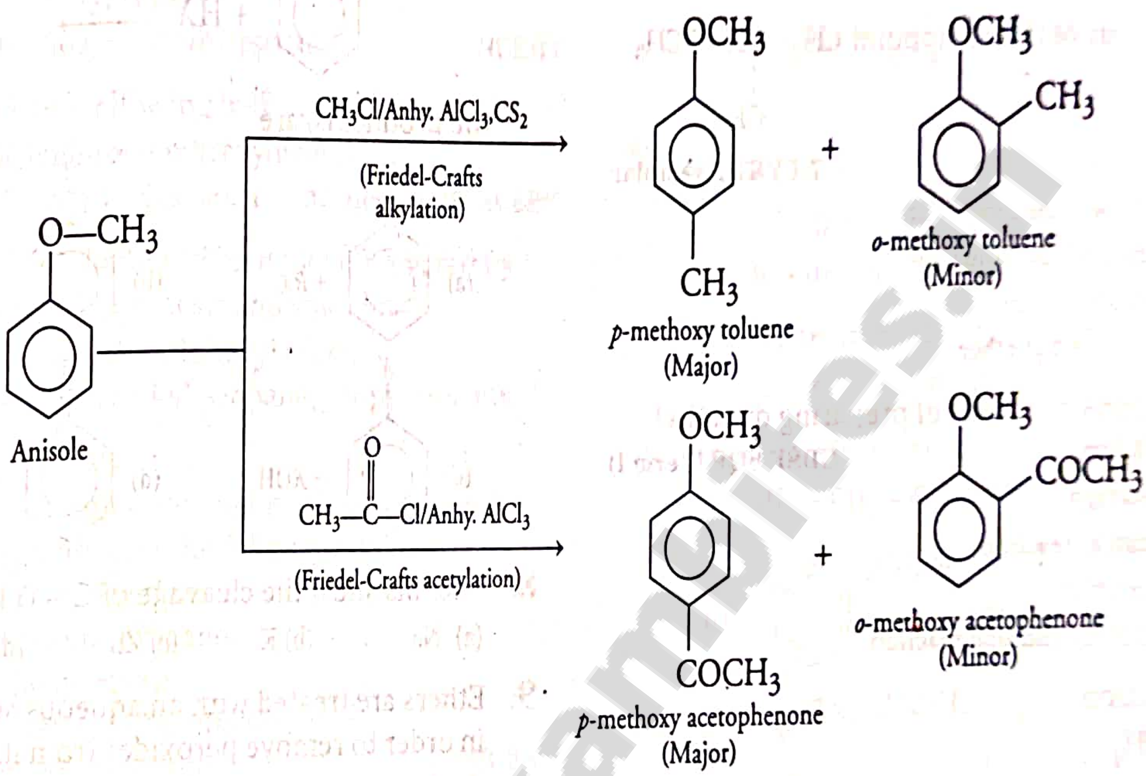


p-bromoanisole (Major) 90% yield

o-bromoanisole (Minor)

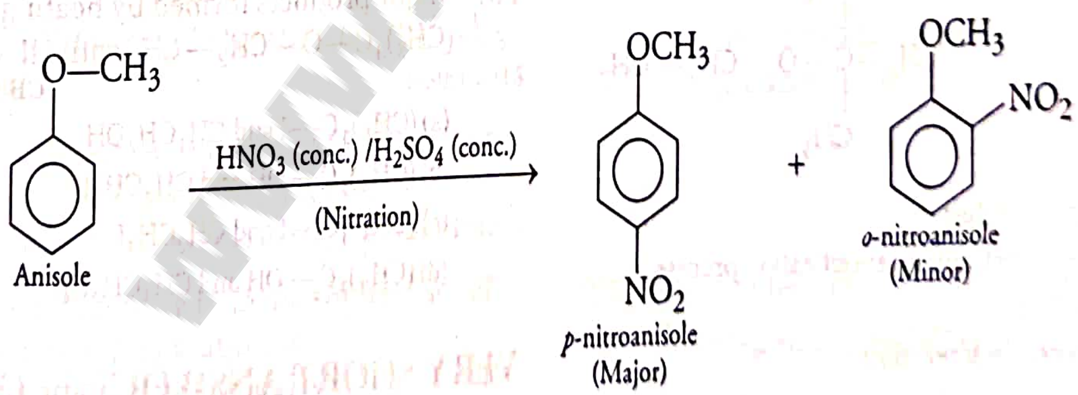
(b) Friedel-Crafts Reaction

Anisole undergoes Friedel-Crafts reaction, i.e. the alkyl and acyl groups are introduced at *o*- and *p*-positions by reaction with alkyl and acyl halides in the presence of anhydrous aluminium chloride (a Lewis acid) as catalyst.



(c) Nitration

Anisole reacts with a mixture of concentrated sulphuric acid and nitric acids to yield a mixture of *ortho* and *para* nitroanisole.



Uses of Ethers

Some of the important uses of ethers are as follows:

(i) Dimethyl ether is used as refrigerant and as solvent at low temperatures.
(ii) Used as an industrial solutions for oils, resins, gums, etc.
(iii) As an extracting solvent in laboratory and industry because of their almost inert nature and good dissolving power.
(iv) Diphenyl ether is used as heat transfer medium because of its high boiling point.

TOPIC PRACTICE 2

OBJECTIVE Type Questions

1. IUPAC name of the compound $CH_3-\underset{\underset{CH_3}{|}}{CH}-OCH_3$ is .... **NCERT Exemplar**

(a) 1-methoxy-1-methylethane
(b) 2-methoxy-2-methylethane
(c) 2-methoxypropane
(d) isopropylmethyl ether

2. Williamson's synthesis of preparing dimethyl ether is a/an **CBSE SQP (Term I)**

(a) S_N1 reaction
(b) elimination reaction
(c) S_N2 reaction
(d) nucleophilic addition reaction

3. The reaction,

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-ONa + CH_3CH_2Cl \xrightarrow[-NaCl]{} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-CH_2-CH_3$$

is called

(a) Williamson synthesis
(b) Williamson continuous etherification process
(c) Etard reaction
(d) Gattermann-Koch reaction

4. Ethers have a net dipole moment because

(a) C—O bonds in ethers are non-polar
(b) C—O bonds in ethers are polar
(c) C—C bonds in ethers are polar
(d) C—C bonds in ethers are non-polar

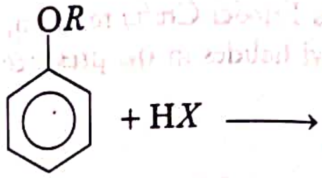
5. The C—O—C bond angle in the ether molecule is **CBSE 2021 (Term I)**

(a) 111° (b) 90°
(c) 120° (d) 180°

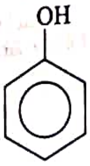
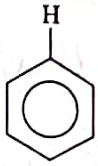
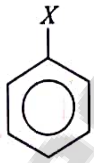
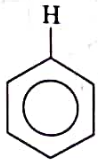
6. The large difference in the boiling points of alcohols and ethers is due to the presence of

(a) van der Waals' forces in alcohols
(b) dipole-dipole interactions in alcohols
(c) hydrogen bonding in alcohols
(d) ion-ion interaction in alcohols

7. In the given reaction,



the product is/are

(a)  + *RX*
(b)  + *RX*
(c)  + *R*OH
(d)  + *ROX*

8. Phenols show the cleavage of C— O bond with

(a) Na (b) K (c) Zn (d) Ca

9. Ethers are treated with an aqueous solution of *A* in order to remove peroxides from it. Identify the '*A*' from the following options.

(a) KI (b) Br_2
(c) KCNS (d) $Na_2S_2O_3$

10. Major products formed by heating $(CH_3)_3C-O-CH_2-CH_3$ with HI are **CBSE 2021 (Term I)**

(a) $(CH_3)_3C-I$ and CH_3CH_2OH
(b) $(CH_3)_3C-OH$ and CH_3CH_2I
(c) $(CH_3)_3C-I$ and CH_3CH_2I
(d) $(CH_3)_3C-OH$ and CH_3CH_2OH

VERY SHORT ANSWER Type Questions

11. Write the IUPAC name of the given compound.

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-CH_2-CH_3$$

All India 2015

12. Write the equation involved in the Williamson's ether synthesis. **All India 2014, 2013**

13. Give reason: $(CH_3)_3C-O-CH_3$ on reaction with HI gives $(CH_3)_3C-I$ and CH_3-OH as the main products and not $(CH_3)_3C-OH$ and CH_3-I. **All India 2015**

14. How do you convert phenol to anisole? **Delhi 2015**

15. Dimethyl ether is completely soluble in water but diethyl ether is soluble in water to small extent. Why?

SHORT ANSWER Type I Questions

16. Draw the structures of the compounds whose IUPAC names are as follows:
(i) 1-ethoxypropane
(ii) 2-ethoxy-3-methylpentane **NCERT**

17. Explain the following with an example.
(i) Williamson's ether synthesis
(ii) Unsymmetrical ether **All India 2013; NCERT**

18. Select the ether which cannot be prepared by Williamson's synthesis and state why?
Divinyl ether, dicyclohexyl ether, 1-propoxy-2-methyl propane, propyl -*sec*-butyl ether.

19. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis.
(i) 1-propoxypropane
(ii) Ethoxybenzene
(iii) 2-methoxy-2-methylpropane
(iv) 1-methoxyethane **NCERT**

20. Give the mechanism of preparation of ethoxy ethane from ethanol. **Delhi 2013 C**

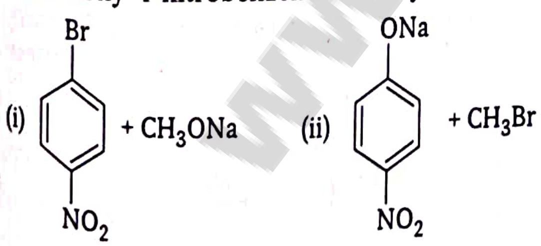
Or Write the mechanism of the following reaction:

$$2CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2—O—CH_2CH_3$$

Delhi 2015

21. Write the reaction of Williamson's synthesis of 2-ethoxy-3-methylpentane, starting from ethanol and 3-methylpentan-2-ol. **NCERT Intext**

22. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?



NCERT Intext

23. Give reason for the higher boiling point of ethanol in comparison to methoxy methane. **NCERT**

Or Explain why alcohols and ethers of comparable molecular mass, have different boiling points? **NCERT Exemplar**

24. Explain why O=C=O is non-polar while R—O—R is polar? **NCERT Exemplar**

25. Write the mechanism of the reaction of HI with methoxy methane. **NCERT**

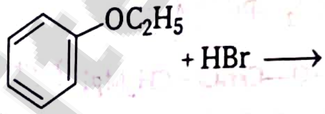
26. Write the mechanism of the following reaction.

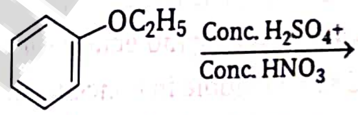
$$2CH_3CH_2OH \xrightarrow[443\ K]{conc.\ H_2SO_4} CH_3CH_2—O—CH_2—CH_3$$

Delhi 2016

27. Explain the fact that in aryl alkyl ether,
(i) the alkoxy group activates the benzene ring towards electrophilic substitution and
(ii) it directs the incoming substituents to *ortho* and *para*-positions in benzene ring. **NCERT**

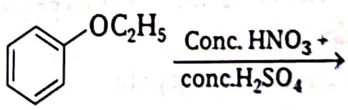
28. Predict the products of the following reactions:
(i) $CH_3—CH_2—CH_2—O—CH_3 + HBr \longrightarrow$

(ii) 

(iii) 

(iv) $(CH_3)_3C—OC_2H_5 \xrightarrow{HI}$

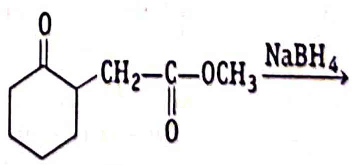
29. (i) Convert propanol to 1-propoxy propane.
(ii) Give the structure and IUPAC name of the major product, obtained in the following reaction:

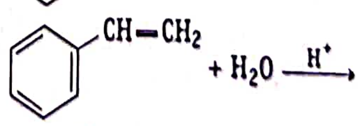


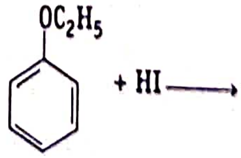
30. State the products of the following reactions:
(i) $CH_3CH_2CH_2CH_2OCH_3 + HBr \longrightarrow$
(ii) $C_2H_5—O—C(CH_3)_3 \xrightarrow{HI}$

SHORT ANSWER Type II Questions

31. Write the structures of the main products in the following reactions: **CBSE 2018**

(a) 

(b) 

(c) 

32. (i) Why phenol is more acidic than ethanol?

(ii) Write the mechanism of acid dehydration of ethanol to yield ether :

$$2CH_3CH_2OH \xrightarrow[413\ K]{H^+} CH_3CH_2OCH_2CH_3$$

All India 2017 C

33. (i) What happens when $CH_3—O—CH_3$ is heated with HI?

(ii) Explain mechanism for hydration of acid catalyzed ethene:

$$CH_2{=}CH_2 + H_2O \xrightarrow{H^+} CH_3—CH_2—OH$$

Delhi 2017 C

34. Complete the following reactions:

(i)
$$\begin{array}{ccc} CH_3CH_2—Br & & Ag\diagdown \\ & + & \quad O \longrightarrow A \\ CH_3CH_2—Br & & Ag\diagup \end{array}$$

(ii) $CH_3—O—CH_2Cl + CH_3MgI \xrightarrow{\text{Dry ether}} B$

35. Compound A having molecular formula $C_4H_{10}O$, is found to be soluble in concentrated sulphuric acid. It does not react with sodium metal or potassium permanganate.

On heating with excess of HI, it gives a single alkyl halide. Deduce the structure of compound A and explain all the reactions.

36. Write the equation for the reaction of hydrogen iodide with

(i) 1-propoxy propane

(ii) methoxy benzene and

(iii) benzyl ethyl ether **NCERT**

37. Illustrate with examples, the limitations of the Williamson's synthesis for the preparation of certain types of ethers. **NCERT**

38. The following is not an appropriate reaction for the preparation of *tert*-butyl methyl ether:

$$CH_3ONa + (CH_3)_3\ C—Cl \longrightarrow (CH_3)_3\ C—OCH_3$$

(i) What would be the major product of the given reaction?

(ii) Write a suitable reaction for the preparation of *tert*-butyl methyl ether, specifying the names of reagents used. Justify your answer in both cases.

39. How is 1-propoxy propane synthesised from propan-1-ol ? Write the mechanism of this reaction. **NCERT**

LONG ANSWER Type Questions

40. (i) Predict the product(s) of the following reaction

$$C_6H_5COCH_3 \xrightarrow{C_6H_5MgBr} A \xrightarrow{H^+/H_2O} B$$

(ii) Explain why anisole does not undergo nucleophilic substitution reactions?

41. Preparation of ethers by acid-catalysed dehydration of secondary and tertiary alcohols is not a suitable method. Give reason. **NCERT**

42. Write equation of the following reactions. **NCERT**

(i) Friedel-Crafts reaction (alkylation in anisole)

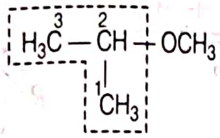
(ii) Nitration of anisole

(iii) Bromination of anisole in ethanoic acid medium

(iv) Friedel-Crafts (acetylation of anisole)

HINTS AND EXPLANATIONS

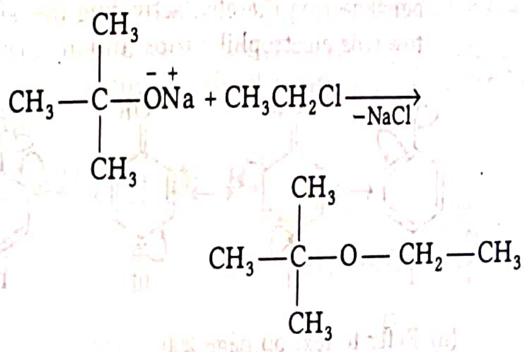
1. (c)



IUPAC name of the above compound is 2-methoxypropane and correct option is (c).

2. (c) In Williamson's synthesis alkoxide ion reacts with primary alkyl halide in a single step to form ether. Hence, it is an S_N2 reaction.

3. (a) The reaction of alkyl halides with sodium alkoxide or sodium phenoxide to form ethers is called Williamson synthesis. Here, in this reaction alkyl halide should be primary and alkoxide, may be bulkier as shown below,



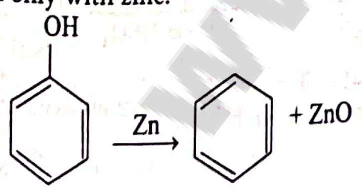
4. (b) The C–O bonds in ethers are polar and thus, ethers have a net dipole moment.

5. (a) The C—O—C bond angle in an ether is 111°.

6. (c) The large difference in the boiling points of alcohols and ethers is due to the presence of H-bonding interaction in alcohols.

7. (a) Alkyl aryl ethers are cleaved at the alkyl oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide.

8. (c) The reactions involving cleavage of C–O bond takes place only in alcohols. Phenols show this type of reaction only with zinc.



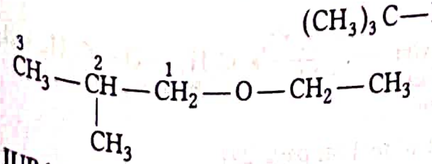
9. (a) KI is added to remove peroxides from Ethers. Ether peroxide oxidises KI into I_2 and itself gets reduced to ether.

$$2I^- \longrightarrow I_2 + 2e^-$$

$$\text{Ether peroxide} + 2e^- \longrightarrow \text{Ether} + O_2$$

10. (a) $(CH_3)_3C{-}O{-}CH_2{-}CH_3 + HI \longrightarrow (CH_3)_3C{-}I + CH_3CH_2OH$

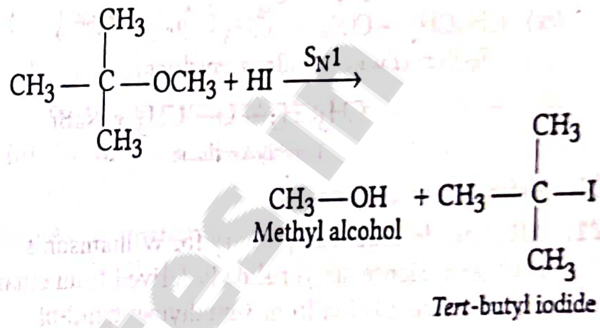
11.



IUPAC Name 1-ethoxy-2-methylpropane

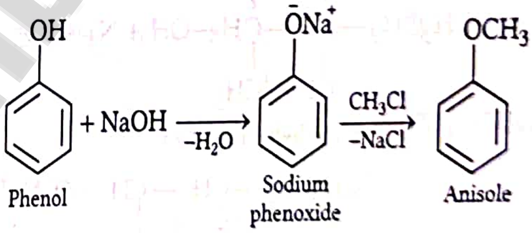
12. $2CH_3X + CH_3\ddot{O}Na \longrightarrow CH_3OCH_3 + NaX$

13. In case of unsymmetrical ethers having two different alkyl groups, the alcohol and the alkyl halide formed depends on the nature of the alkyl group. If one of the alkyl group is tertiary, the alkyl halide is formed from the tertiary alkyl group.



This is due to the reason that the reaction occurs *via* S_N1 mechanism and the formation of products is controlled by the stability of the carbocation.

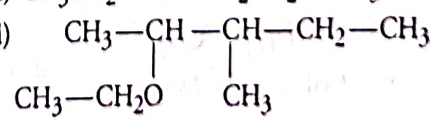
14.



15. Both dimethyl ether and diethyl ether form weak hydrogen bonds with water which accounts for their solubility in water. However, in diethyl ether, the hydrophobic hydrocarbon part is larger than dimethyl ether and therefore, limits the hydrogen bond formation.

16. (i) $CH_3CH_2{-}O{-}CH_2CH_2{-}CH_3$

(ii)



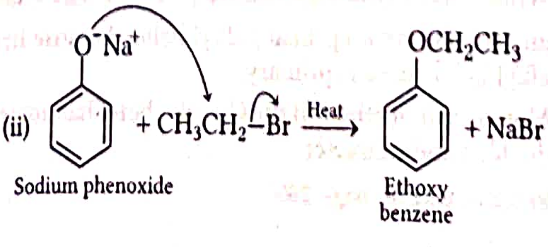
17. (i) **Williamson's ether synthesis** Refer to text on pages 287 and 288.

(ii) **Unsymmetrical ether** Refer to text on page 288.

18. Refer to text on page 288.

19. (i) $\underset{\text{Sodium propoxide}}{CH_3CH_2CH_2O^-{-}Na^+} + \underset{\text{1-bromopropane}}{CH_3CH_2CH_2{-}Br} \xrightarrow{\text{Heat}} \underset{\text{1-propoxypropane}}{CH_3CH_2CH_2{-}O{-}CH_2CH_2CH_3} + NaBr$

(ii)



(iii) $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O^-Na^+ + CH_3-Br \xrightarrow{\text{Heat}}$
Sodium-2-methyl-2-propoxide

$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OCH_3 + NaBr$
2-methoxy-2-methylpropane

(iv) $CH_3CH_2-\overset{-}{O}\overset{+}{Na} + CH_3-Br \xrightarrow{\text{Heat}}$
Sodium ethoxide Bromomethane

$CH_3CH_2-O-CH_3 + NaBr$
1-methoxyethane

20. Refer to text on page 287.

21. Alkyl halide should be primary for Williamson's synthesis. Hence, alkyl halide is derived from ethanol and the alkoxide ion from 3-methylpentan-2-ol.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + HBr \xrightarrow{\Delta} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} + H_2O$$

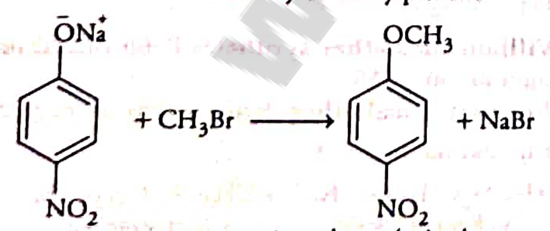
$$\overset{5}{C}H_3\overset{4}{C}H_2-\underset{CH_3}{\underset{|}{\overset{3}{C}H}}-\underset{^1CH_3}{\underset{|}{\overset{2}{C}H}}-OH + Na \longrightarrow$$
3-methylpentan-2-ol

$$2CH_3CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-O^-Na^+ + H_2$$
Sodium-3-methyl-2-pentoxide

$$CH_3CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-O^-Na^+ + CH_3CH_2-Br$$

$$\xrightarrow{S_N2} \overset{5}{C}H_3\overset{4}{C}H_2-\underset{CH_3}{\underset{|}{\overset{3}{C}H}}-\underset{^1CH_3}{\underset{|}{\overset{2}{C}H}}-O-C_2H_5 + NaBr$$
2-ethoxy-3-methylpentane

22.

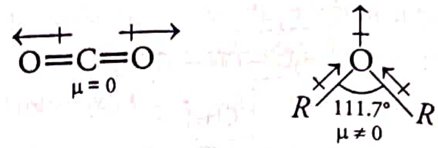


1-methoxy-4-nitrobenzene

This reaction involves the preparation of ether by Williamson's synthesis. It takes place *via* S_N2 attack of an alkoxide ion on primary alkyl halide because here the alkyl halide used is primary.
Moreover in method (i) the C—Br bond has some double bond character.

23. Refer to text on page 288.

24. CO_2 is a linear molecule. The dipole moment of two $C=O$ bonds are equal and opposite. Hence, they cancel each other. So, the dipole moment of CO_2 is zero and it is a non-polar molecule.

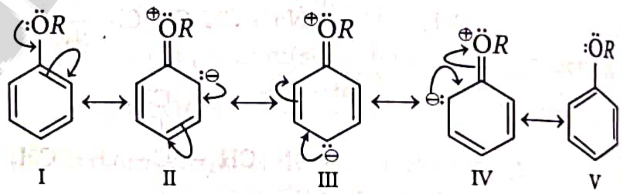


While for ethers, two dipoles are pointing in the same direction. These two dipoles do not cancel the effect of each other. Therefore, there is a finite resultant dipoles and hence, $R-O-R$ is a polar molecule.

25. Refer to text on page 289.

26. Refer to text on page 287.

27. (i) In aryl alkyl ethers, $+R$-effect of the alkoxy group ($-OR$) increases the electron density on the benzene ring thereby, activating the benzene ring towards electrophilic substitution reactions.

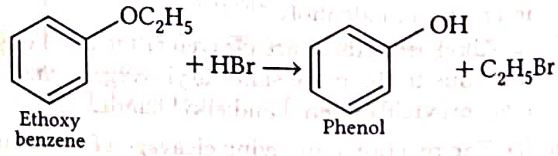


(ii) Refer to text on page 290

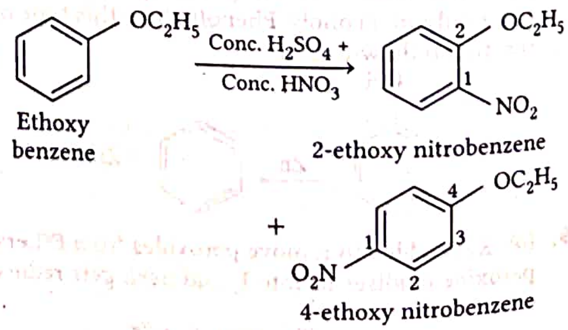
28. (i) $\underset{\text{Methoxy propane}}{CH_3-CH_2-CH_2-O-CH_3} + HBr \longrightarrow$

$$\underset{\text{Propanol}}{CH_3-CH_2-CH_2-OH} + CH_3Br$$

(ii)



(iii)



(iv) $\underset{t\text{-butyl ethyl ether}}{(CH_3)_3C-OC_2H_5} \xrightarrow{HI} \underset{t\text{-butyl iodide}}{(CH_3)_3C-I} + \underset{\text{Ethanol}}{C_2H_5OH}$

29. (i) $\underset{\text{Propanol (Excess)}}{C_3H_7OH} \xrightarrow[413\text{ K}]{\text{Conc. } H_2SO_4} \underset{\text{Propoxy propane}}{C_3H_7-O-C_3H_7} + H_2O$

(ii) Refer to text on page 291.

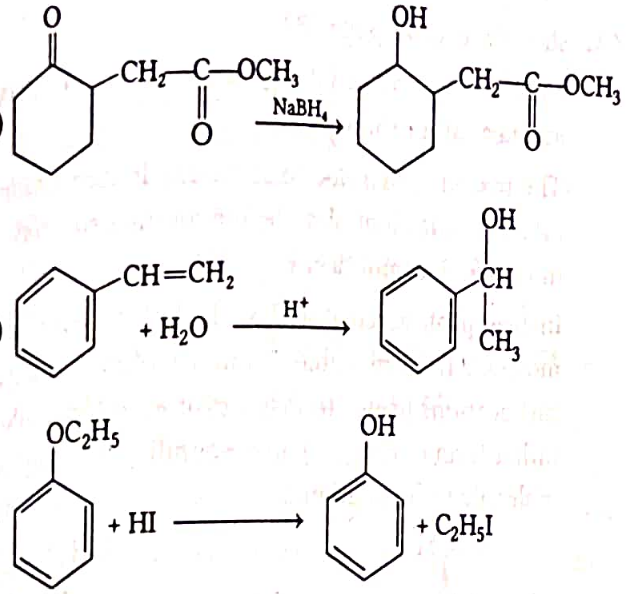
30. Refer to text on page 289.

31.

(a)

(b)

(c)



32. (i) Due to resonance, phenoxide ion is more stable than phenol whereas there is no resonance in alkoxide ion (explained with the help of resonating structures on page 268.

(ii) $CH_3—CH_2—\ddot{O}—H + H^+ \longrightarrow CH_3—CH_2—\overset{+}{O}(H)—H$

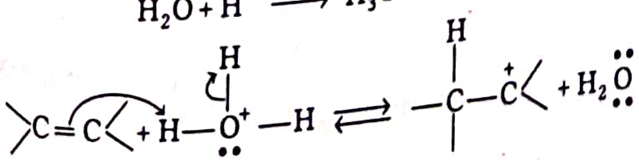
$CH_3CH_2—\ddot{O}(H): + CH_3—CH_2—\overset{+}{O}H_2 \longrightarrow CH_3CH_2—\overset{+}{O}(H)—CH_2CH_3 + H_2O$

$CH_3CH_2—\overset{+}{O}(H)—CH_2CH_3 \longrightarrow CH_3CH_2—O—CH_2CH_3 + H^+$

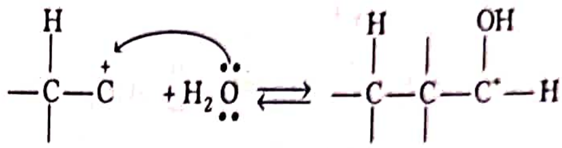
33. (i) $CH_3—O—CH_3 + HI \longrightarrow CH_3—OH + CH_3—I$

(ii) (a) Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

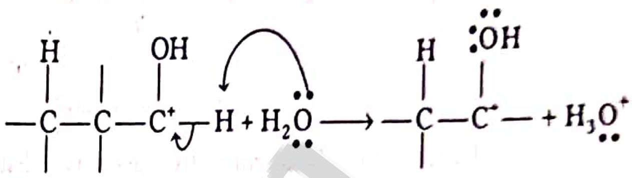
$H_2O + H^+ \longrightarrow H_3O^+$



(b) Nucleophilic attack of water on carbocation.



(c) Deprotonation to form an alcohol.



34. (i) Refer to text on 288.

(ii) Refer to text on 288.

35. (i) As compound A does not react with sodium metal or potassium permanganate, it cannot be an alcohol.

(ii) As compound A dissolves in conc. H_2SO_4, it may be an ether.

(iii) As compound A on heating with excess of HI, gives a single alkyl halide, therefore compound A must be a symmetrical ether.

(iv) The only symmetrical ether having molecular formula $C_4H_{10}O$ is diethyl ether. Thus, compound A is diethyl ether, $CH_3—CH_2—O—CH_2—CH_3$.

$CH_3CH_2—O—CH_2CH_3 \xrightarrow{\text{Conc. } H_2SO_4} \left[CH_3—CH_2—\overset{+}{O}(H)—CH_2—CH_3\right]HSO_4^-$

Soluble oxonium salt

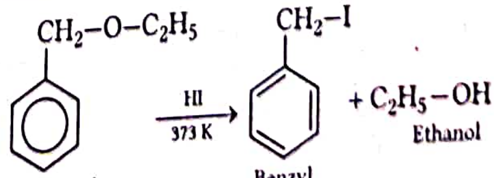
$\underset{\substack{(A)\\ \text{Diethyl ether}}}{CH_3CH_2OCH_2CH_3} \xrightarrow[\Delta]{HI} \underset{\text{Ethyl iodide}}{2\,CH_3CH_2—I}$

36. (i) $\underset{\text{1-propoxy propane}}{CH_3CH_2CH_2—O—CH_2CH_2CH_3} \xrightarrow[373\text{ K}]{HI}$

$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2—OH} + \underset{\text{1-iodopropane}}{CH_3CH_2CH_2—I}$

(ii) Refer to text on page 289.

(iii)



Benzyl ethyl ether — Benzyl iodide — Ethanol

37. (i) Williamson's synthesis is not applicable for tertiary alkyl halides as they yield alkenes instead of ethers. The reaction of CH_3ONa with $(CH_3)_3C—Br$ gives exclusively 2-methylpropene.

$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br + Na-\ddot{\underset{..}{O}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2 + NaBr$$

tert-butyl bromide 2-methyl propene

(ii) Aryl and vinyl halides cannot be used as substrates because of their low reactivity in nucleophilic substitution.

38. Refer to text on page 288.

39. Two methods can be employed for this preparation:

(i) *Via* Williamson's synthesis

(a) $3CH_3CH_2CH_2OH + PBr_3 \longrightarrow 3CH_3CH_2CH_2Br + H_3PO_3$

Propan-1-ol → 1-bromopropane

(b) $2CH_3CH_2CH_2OH + 2Na \longrightarrow 2CH_3CH_2CH_2O^-Na^+ + H_2$

Propan-1-ol → Sodium propoxide

$$\underset{\text{Sodium propoxide}}{CH_3CH_2CH_2O^-Na^+} + \underset{\text{1-bromopropane}}{CH_3CH_2CH_2-Br} \xrightarrow[\text{Heat}]{\text{Dry ether}} \underset{\text{1-propoxypropane}}{CH_3CH_2CH_2-O-CH_2CH_2CH_3} + NaBr$$

(ii) By the dehydration of propan-1-ol with conc. H_2SO_4 at 413 K

$$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + H^+ \longrightarrow \underset{\text{Protonated propan-1-ol}}{CH_3CH_2CH_2-\overset{+}{\ddot{O}}H_2}$$

$$CH_3CH_2CH_2-\ddot{\underset{..}{O}}H + CH_3CH_2CH_2-\overset{+}{\ddot{O}}H_2 \xrightarrow[-H_2O,\,-H^+]{413\text{ K}} \underset{\text{1-propoxypropane}}{CH_3CH_2CH_2-O-CH_2CH_2CH_3}$$

40. (i) Refer to text on page 266.

(ii) Refer to text on page 290.

41. Refer to text on page 287.

Under acid catalysed dehydration, 2° and 3° alcohols give alkenes rather than ethers.

The reason is that due to steric hindrance, nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur.

Instead protonated 2° and 3° alcohols lose a water molecule to form stable 2° and 3° carbocations. These carbocations prefer to lose a proton to form alkenes rather than undergoing nucleophilic attack by alcohol molecule to form ethers.

$$\underset{\text{Propan-2-ol (2° alcohol)}}{CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-OH} \xrightarrow{H^+} \underset{\text{Protonated propan-2-ol}}{CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{+}{O}H_2} \xrightarrow{-H_2O} \underset{\textit{iso}\text{-propyl carbocation}}{CH_3-\overset{CH_3}{\overset{|}{\overset{+}{C}H}}}$$

$$\underset{\text{(Not formed)}}{CH_3-\overset{CH_3}{\overset{|}{C}H}-O-\overset{CH_3}{\overset{|}{C}H}-CH_3} \xleftarrow[-H^+]{CH_3CHOHCH_3}$$

$$\underset{\textit{iso}\text{-propyl carbocation}}{CH_3-\overset{CH_3}{\overset{|}{C}H^+}} \xrightarrow[-H^+]{} \underset{\text{Propene}}{CH_3-CH=CH_2}$$

42. Refer to text on pages 290 and 291.

SUMMARY

- Alcohols are hydroxy organic compounds of the alkanes with general formula $C_nH_{2n+2}O$ or $C_nH_{2n+1}OH$.
- The class of organic compounds which contain a hydroxyl group, attached directly to an aromatic ring, are known as phenols.
- Alcohols are named by replacing the terminal '–e' of the corresponding alkane name by –'ol'
- Alcohols exhibit chain, position, functional and optical isomerism.

Methods of Preparation of Alcohols

Method	Reaction involved
1. Hydration of alkenes	$(CH_3)_2C=CH_2 + H_2O \longrightarrow (CH_3)_3C—OH$
2. Hydroboration oxidation	$3R—CH=CH_2 + BH_3 \xrightarrow[\text{DIGLYME}]{\text{THF or}} (RCH_2CH_2)_3B \xrightarrow{H_2O_2} RCH_2CH_2OH$
3. Reduction of aldehydes, ketones, acids and acid derivatives	$LiAlH_4$ or H_2/Ni, Pt, Pd, 250°C reduces; $NaBH_4$ reduces; $—CHO, —COCl, >C=O, —CO_2R$ to $—CH_2OH$
4. From Grignard's reagent	$\overset{-}{R}\overset{+}{Mg}X + >C=O \longrightarrow >C(R)—\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O} >C(R)—OH$

Methods of Preparation of Phenols

Methods	Reaction involved
1. Dow process (by hydrolysis)	$PhX \xrightarrow[340°C, 150\ atm]{aq.NaOH} PhO^-Na^+ \xrightarrow{H_2O/H^+} PhOH$
2. Cumene process	$PhCH(CH_3)_2 \xrightarrow[H_2O/H^+]{O_2\ catalyst} PhOH + CH_3COCH_3$
3. From diazonium salts	$PhN^+ \equiv NX^- \xrightarrow{H_2O/H^+} PhOH + N_2\uparrow + HX$
4. Fusion of alkali metal salt of sulphonic acid	$PhSO_3^-Na^+ + NaOH \xrightarrow{Fuse} PhO^-Na^+ \xrightarrow{H_2O/H^+} PhOH$
5. From Grignard's reagent	$PhMgBr \xrightarrow{[O]} PhOMgBr \xrightarrow{H_2O/H^+} PhOH$

Physical Properties of Alcohols

- Lower alcohols are colourless, toxic liquids whereas the higher members are waxy solids.
- The boiling point of alcohol is always higher than the corresponding ether, hydrocarbon and haloalkane due to the presence of hydrogen bonding.

Physical Properties of Phenols

- Colourless, crystalline, deliquescent liquid or solid.
- Characteristic carbolic odour, sparingly soluble in water.
- Capable of forming intermolecular H-bonding with water and among themselves.

Distinction between 1°, 2° and 3° Alcohols

Name of the test and procedure	1° alcohol	2° alcohol	3° alcohol
Lucas test Alcohol is treated with Lucas reagent (equimolar mixture of anhy. $ZnCl_2$ and conc.HCl)	Does not react	Produces turbidity after 5 min	Produces turbidity immediately
Dehydrogenation Cu or Ag are used for dehydrogenation	Produces aldehyde	Produces ketone	Dehydrated to give alkene

- **Methanol** is a colourless liquid and boils at 373 K. It is highly poisonous in nature. Ingestion of even small quantities of methanol is hazardous and large quantities causes even death.
- **Ethanol** is a good industrial solvent. It is a colourless liquid with boiling point 351 K. It is used as a solvent in paint industry.

Ethers

- Ethers are the organic compounds having two alkyl groups bounded to an oxygen atom with general molecular structure of $R—O—R'$.
- IUPAC nomenclature $\underbrace{R}_{\substack{\text{Alkane}\\\text{(larger group)}}} — \underbrace{O—R'}_{\substack{\text{Alkoxy}\\\text{(smaller group)}}}$, $CH_3O—CH_2CH_3$ Methoxy ethane (right) ethoxy methane (wrong)

Preparation of Ethers

1. By dehydration of alcohols	$2ROH \xrightarrow[\Delta\ 413K]{H_2SO_4} R—O—R + H_2O$
2. Williamson's synthesis	$R—Br + R'ONa \longrightarrow ROR' + NaBr$ (R is generally 1°, or benzyl with 3° R, alkene is the major product)
3. Reaction of alkyl halides with dry silver oxide	$2RX + Ag_2O \xrightarrow{\Delta} R—O—R + 2AgX$
4. From Grignard reagent	$CH_3OCH_2Cl + CH_3MgI \xrightarrow{\text{Dry ether}} CH_3OCH_2CH_3 + Mg(Cl)I$

Physical Properties

- Colourless liquids with ethereal smell, lower boiling point than isomeric alcohols.
- Ethers upto three carbon atoms are soluble in water due to the formation of intermolecular H-bonding.

CHAPTER PRACTICE

OBJECTIVE Type Questions

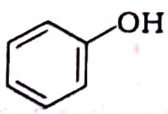
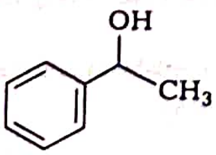
1 In ethers, the two bond pairs and two lone pairs of electrons on oxygen are arranged in a
(a) planar arrangement
(b) tetrahedral arrangement
(c) trigonal bipyramidal arrangement
(d) linear arrangement

2 The reagent(s) used for the reduction of aldehydes and ketone into alcohols is/are
(a) finely divided metals such as Pt/Pd/Ni
(b) sodium borohydride
(c) lithium aluminium hydride
(d) All of the above

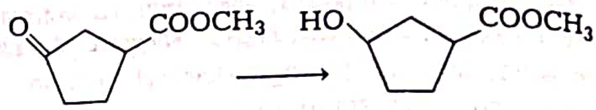
3 During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4, the initiation step is CBSE SQP (Term I)
(a) protonation of alcohol molecule
(b) formation of carbocation
(c) elimination of water
(d) formation of an ester

4 Salicylic acid and phenol can be distinguished by the use of
(a) bromine water
(b) neutral $FeCl_3$
(c) 5% NaOH solution
(d) $NaHCO_3$ solution

5 The electrophile used in Reimer-Tiemann reaction is
(a) $CCl_3^{\oplus}$ (b) $:CCl_2$ (c) $Cl^{\oplus}$ (d) H_2O

6 Identify the secondary alcohols from the following set:
(i) $CH_3CH_2CH(OH)CH_3$
(ii) $(C_2H_5)_3COH$
(iii) 
(iv) 

CBSE SQP (Term I)
(a) (i) and (iv) (b) (i) and (iii)
(c) (i) and (ii) (d) (i), (iii) and (iv)

7. 

Which of the following reagents should be used to carry out the above conversion? CBSE 2021 (Term I)
(a) $LiAlH_4$
(b) $NaBH_4$
(c) Zn-Hg/HCl
(d) $KMnO_4$

8. Lucas reagent produces cloudiness immediately with CBSE 2021 (Term I)
(a) $CH_3-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$
(b) $CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$
(c) $CH_3-CH_2-CH_2-OH$
(d) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-OH$

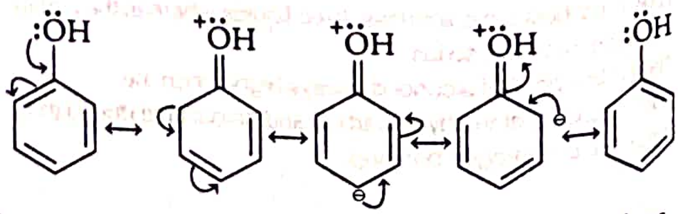
CASE BASED Type Questions

Case I

Phenols undergo electrophilic aromatic substitution reaction readily because —OH group attached to the benzene ring activates the benzene ring towards electrophilic substitution reaction.

Further, it directs the incoming group to *ortho* and *para* positions in the ring as these positions become electron rich due to the resonance effect.

The delocalisation of electrons (or resonance) can be represented as



Common electrophilic aromatic substitution reactions taking place in phenol are nitration, sulphonation and halogenation.

The following questions are multiple choice questions. Choose the most appropriate answer :

9 Name the reagent used in the bromination of phenol to give 2, 4, 6-tribromophenol.

(a) bromine (b) *aq.* bromine

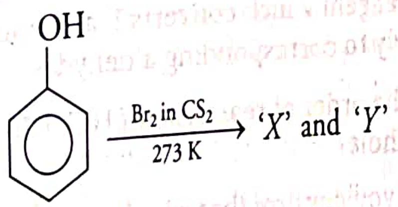
(c) HBr (d) NaBr

10 What are the products obtained on reaction of phenol with dil. HNO_3?

(a) *p*-nitrophenol (b) *o*-nitrophenol

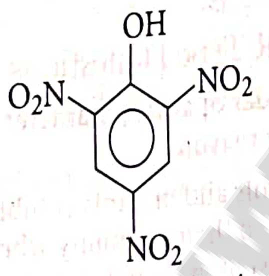
(c) *m*-introphenol (d) Both (a) and (b)

11 Complete the reaction,



	X	Y
(a)	*o*-bromophenol	*p*-bromophenol
(b)	*m*-bromophenol	*p*-bromophenol
(c)	*o*-bromophenol	*m*-bromophenol
(d)	None of the above	

12 Write the name of structure



2,4,6-trinitrophenol

(a) salicylic acid (b) citric acid

(c) folic acid (d) picric acid

Or Which will prefer to undergo intramolecular H-bonding?

(a) *o*-nitrophenol

(b) *p*-nitrophenol

(c) *m*-nitrophenol

(d) None of the above

Case II

In phenol, OH-group directly attached to sp^2-hybridised carbon of benzene ring acts as a electron withdrawing group and is responsible for the acidic nature of phenol. Due to this, the lone pair of electrons of O—H are involved in resonance with C-atoms of benzene ring. As a result of resonance, the oxygen atom acquires a partial positive charge. This weakens the O—H bond and, thus facilitates the release of a proton.

As a result, phenols behave as Bronsted acids. The reaction of phenol with aqueous NaOH indicates that phenols are stronger acids than alcohols.

The reactions of phenol with metals such as Na, Al and NaOH indicate its acidic nature.

In the question that follow Assertion and Reason are given. Reason is purported to the explaination for Assertion. Study carefully and then mark your answers, according to the codes given below.

Marks your answer as :

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

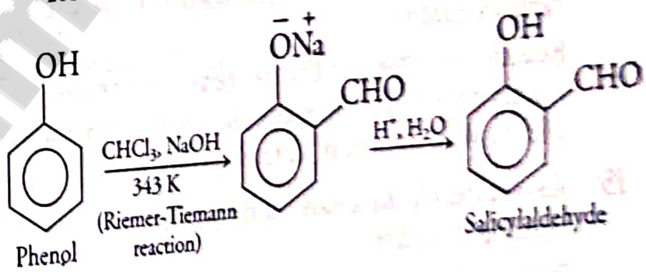
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

13 **Assertion** The reaction of phenol with chloroform in presence of aq. NaOH gives salicylic acid.

Reason

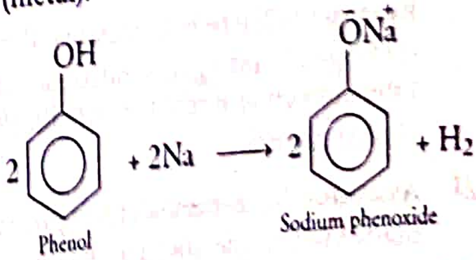


Or **Assertion** Phenol is more stronger acid than ethanol.

Reason Phenoxide ion is more resonance stabilised than phenol.

14 **Assertion** Phenol is acidic in nature as it reacts with Na (metal).

Reason



15 **Assertion** *o*-nitrophenol, *o*-cresol and phenol in the increasing order of acidic strength.

Reason *o*-nitrophenol > phenol > *o*-cresol.

16 **Assertion** The intermediate formed after the loss of H^+ ion from phenol.

Reason Phenoxide ion is formed as intermediate.

ASSERTION and REASON

■ **Directions** (Q. Nos. 17-22) *In the following questions, an Assertion (A) is followed by a corresponding Reason (R) Use the following keys to choose the appropriate answer.*

(a) Both (A) and (R) are correct, (R) is the correct explanation of (A).
(b) Both (A) and (R) are correct, (R) is not the correct explanation of (A).
(c) (A) is correct; (R) is incorrect.
(d) (A) is incorrect; (R) is correct.

17 **Assertion** (A) Carbon oxygen bond length of phenol is slightly less than that of methanol.

Reason (R) There exist a partial double bond character and sp^2-hybridisation of carbon to which oxygen is attached in phenol.

18 **Assertion** (A) In alcohols, the boiling point decreases with decrease in branching of the carbon chain.

Reason (R) There is the decrease in van der Waals' forces between the number of carbon atoms with decrease in the surface area.

19 **Assertion** (A) Alcohols and phenols are soluble in water.

Reason (R) There occurs a dipole-dipole interaction of OH group of alcohol and phenol with water molecules which is responsible for their solubility in water.

20 **Assertion** (A) *o*-nitrophenol is less volatile than *p*-nitrophenol.

Reason (R) There is intramolecular hydrogen bonding in *o*-nitrophenol and intermolecular hydrogen bonding in *p*-nitrophenol.

21 **Assertion** (A) Bromination of phenol takes place even in the absence of Lewis acid.

Reason (R) In phenol, OH group attached to benzene ring has highly deactivating effect.

22 **Assertion** (A) Addition reaction of water to but-1-ene in acidic medium yields butan-2-ol.

Reason (R) Addition of water in acidic medium proceeds through the formation of primary carbanion.

VERY SHORT ANSWER Type Questions

23 What is the IUPAC name of the following compounds?

(i) $\underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$ (ii) $CH_3CH_2CH_2-OCH_2CH_3$

24 Name the starting material used in the industrial preparation of phenol.

25 Give reason.
The boiling points of alcohols decreases with increase in branching of the alkyl chain.

26 Name a reagent which converts 1° alcohols exclusively to corresponding aldehydes.

27 What is the order of reactivity of HCl, HBr and HI with alcohols?

28 How will you confirm that whether a given –OH group is alcoholic or phenolic?

29 Why aryl halides cannot be used for the formation of ethers?

30 Why are higher ethers insoluble in water?

31 Name the products obtained when anisole is heated with HI.

SHORT ANSWER Type I Questions

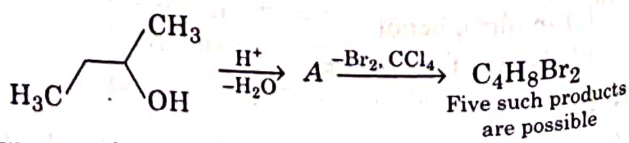
32 What is the order of acidic character of 1°, 2° and 3° alcohols? Give reason.

33 Why are alcohols and phenols soluble in water? What happens to their solubility when bulky alkyl groups are present in them?

34 What is the main product obtained when vapours of *t*-butyl alcohol are passed over copper at 573 K? Give reaction also.

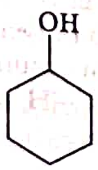
35 Name the compound with molecular formula C_7H_8O which on treatment with Br_2 water, readily gives a precipitate of $C_7H_5OBr_3$.

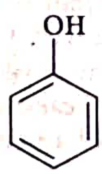
36 In the reaction,



How many isomer(s) of *A* is/are possible?

37 How will you distinguish between the following compounds?



and


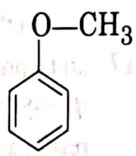
38 Methyl tertiary butyl ether is an important additive of gasoline. How it can be prepared using Williamson's synthesis?

39 What happens when anisole is heated with HI?

40 *Iso*-propyl benzene is oxidised in the presence of air to compound *A*. When compound *A* is treated with dilute mineral acid, which aromatic compound is formed?

41 Explain why alcohols do not react with NaBr but when H_2SO_4 is added, they form alkyl bromides?

42 Arrange the following compounds in the decreasing order of their boiling points.

$C_2H_5—O—C_2H_5$, $CH_3—O—C_2H_5$, 

(I) (II) (III)

SHORT ANSWER Type II Questions

43 Give the reaction of alcohols with phosphorus trihalides and hydrogen halides.

44 Complete the following equations and name the products formed.

(i) $C_6H_5OH + Br_2 \xrightarrow{H_2O}$ (ii) $(CH_3)_2C{=}O \xrightarrow{LiAlH_4}$

(iii) $C_6H_5OH + CHCl_3 \xrightarrow[340\ K]{aq.\ NaOH}$

45 How will you convert

(i) phenol to 4-bromophenol?

(ii) phenol to 2-hydroxy benzoic acid?

46 (i) How will you distinguish between the following pair by suitable chemical tests? butan-1-ol and butan-2-ol

(ii) Complete the following reaction:

$HOCH_2—CHOH—CH_2OH \xrightarrow{HI}$

47 Why 2,4,6-trinitrophenol is a strong acid? How is it prepared from phenol?

48 How does Lucas reagent help in the distinction of primary, secondary and tertiary alcohols? Discuss the reactions involved.

49 Give the industrial uses of methanol and ethanol.

50 (i) How can diethyl ether be prepared from the following?

(a) Ethyl iodide (b) Ethyl alcohol

Write the chemical equation in each case.

(ii) How is ethyl alcohol obtained from molasses?

LONG ANSWER Type Questions

51 (i) How is phenol obtained from (a) aniline (b) benzene sulphonic acid?

(ii) How it can be converted into (a) salicylaldehyde (b) benzoquinone (c) toluene?

52 (i) Identify the product when

$CH_3CH{=}CH—CH_2—CH_2—\overset{\overset{\large O}{\|}}{C}—CH_3$ reacts with following reagents:

(a) $LiAlH_4/D_2O$

(b) $NaBH_4$

(c) C_2H_5MgBr

(ii) Write the structure and mechanism of the product formation in the following reaction:

$PhCH_2—O—CH\begin{matrix} Ph \\ Ph \end{matrix} \xrightarrow{Conc.HI}$

ANSWERS

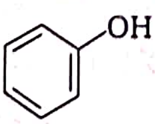
1. (*b*) 2. (*d*)

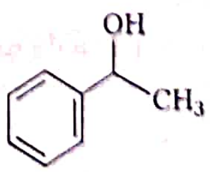
3. (*a*) During dehydration of alcohol to alkene by heating is on conc. H_2SO_4, the initial step is protonation of alcohol molecule.

4. (*d*) 5. (*b*)

6 (*a*) (i) $CH_3CH_2CH(OH)CH_3$ (Secondary)

(ii) $(C_2H_5)_3COH$ (tertiary)

(iii)  (It's phenol and not alcohol)

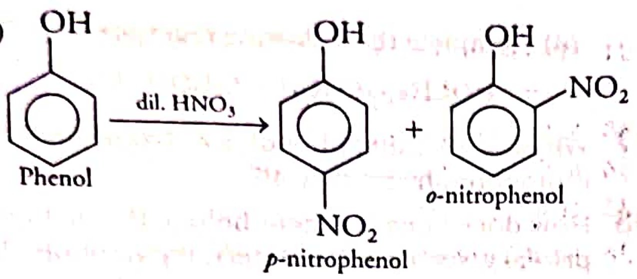
(iv)  (Secondary)

7 (*b*) This conversion can be carry out by the $NaBH_4$ because it can reduce ketone into alcohol.

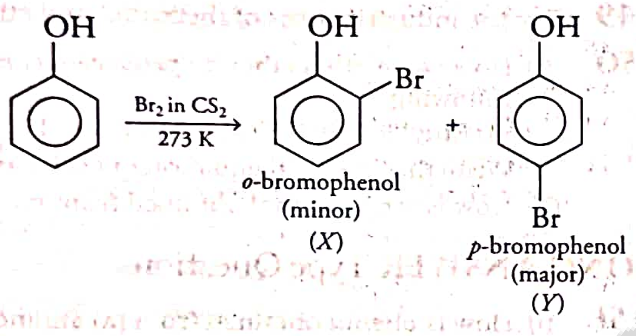
8 (*a*) With Lucas reagent, tertiary alcohols react immediately as they form tertiary carbocations which are the most stable. Hence, turbidity is observed in seconds.

9 (*b*) Aqueous bromine.

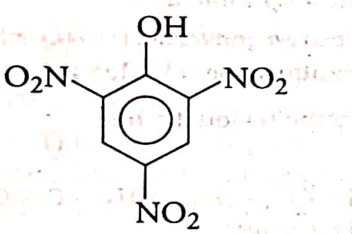
10 (*d*)



11 (*a*)



12 (*d*)

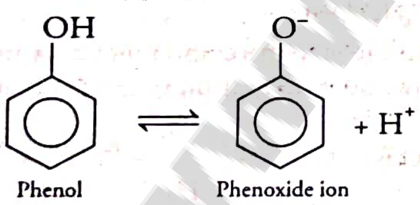


2,4,6-trinitrophenol (Picric acid)

Or (*a*) *o*-nitrophenol.

13 (*d*) A is false but (R) is true.

Or (*a*)



Phenoxide ion is more resonance stabilised than phenol.

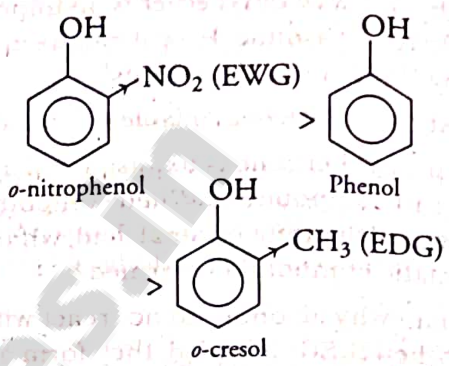
$$\underset{\text{Ethanol}}{C_2H_5OH} \rightleftharpoons \underset{\text{Alkoxide ion}}{CH_3CH_2-O^-} + H^+$$

No, resonance stabilisation for alcohol or alkoxide ion.

Both (A) and (R) are true and (R) is the correct explanation of (A).

14 (*a*) Both (A) and (R) are correct and (R) is the correct explanation of (A).

15 (*a*)



Both (A) and (R) are correct and (R) is the correct explanation of (A).

16 (*a*) Both (A) and (R) are corect and (R) is correct explanation of (A).

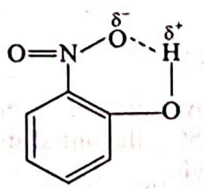
17 (*a*) In phenols, the — OH group is attached to sp^2-hybridised carbon atom of an aromatic ring. As a result, a partial double bond exist between C—O bond. So, the carbon oxygen bond length (136 pm) in phenol is slightly less than that in methanol. Hence, both (A) and (R) are correct and R is the correct explanation of (A).

18 (*d*) The boiling point of alcohols and phenols increases with increase in the number of carbon atoms (increase in van der Waals' forces). In alcohols, the boiling point decreases with increase of branching in carbon chain (because of decrease in van der Waals' forces with decrease in surface area). Hence, (A) is incorrect but (R) is correct.

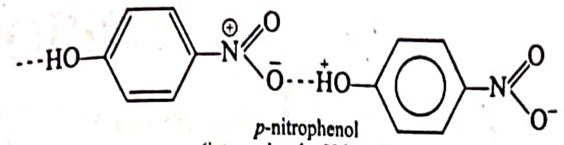
19 (*c*) Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules.

The solubility decreases with increase in size of the alkyl/aryl groups. Several lower molecular mass alcohols are miscible with water in all proportions. Hence, (A) is correct but (R) is incorrect.

20 (*d*) *o*-nitrophenol is more volatile due to intramolecular hydrogen bonding, while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules. Hence, (A) is incorrect but (R) is correct.



o-nitrophenol (intramolecular H-bonding)



p-nitrophenol
(intermolecular H-bonding)

21 (c) In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of OH group attached to the benzene ring. Hence, (A) is correct but (R) is incorrect.

22 (c) Addition of water to but-1-ene in acidic medium yields butan-2-ol. It is as follows :

$$\underset{\text{But-1-ene}}{CH_3-CH_2-CH=CH_2} + H_2O \xrightarrow{H_2SO_4}$$

$$CH_3-CH_2-\underset{\underset{OSO_3H}{|}}{CH}-CH_3 \xrightarrow{H_2SO_4}$$

$$\underset{\text{Butan-2-ol}}{CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3} + H_2SO_4$$

Addition of H_2O to unsymmetrical alkenes takes place in accordance with the Markownikoff's rule *via* the formation of carbocation. Hence, (A) is correct but (R) is incorrect.

23 (i) Propane-1,2,3-triol (ii) Ethoxy propane

24 Cumene is the starting material used in the industrial preparation of phenol.

25 In alcohols, the boiling point decreases with increase of branching in carbon chain because of decrease in van der Waals' forces with decrease in surface area.

26 **Hint** PCC

27 HI > HBr > HCl

28 **Hint** Reaction with $FeCl_3$
Phenol gives positive test while alcohol does not.

29 Aryl halides can not be used for the formation of ethers because they are less reactive foward nucleophilic substitution reactions.

30 Higher ethers are immimiscible with H_2O due to the presence of large hydrocarbon part.

31 Phenols is formed.

32 Refer to text on page 268.

33 Refer to text on page 267.

34 Refer to text on page 271.

35 **Hint** $C_6H_5CH_2OH$

36 **Hint** 2 isomers are possible.

37 **Hint** Phenol gives violet colouration with $FeCl_3$ solution while cyclohexanol does not react.

38 Refer to text on pages 288.

39 Refer to text on page 290.

40 **Hint** Compound is phenol

41 **Hint** OH^- being a strong base is a bad leaving group. When H_2SO_4 is added, protonation of alcohol occurs i.e –OH is converted into $-\overset{+}{O}H_2$.

42 Refer to text on page 288.

43 Refer to text on pages 269 and 270.

44 (i) Refer to text on page 272.
(ii) Refer to text on page 265.
(iii) Refer to text on page 272.

45 (i) Refer to text on page 272.
(ii) Refer to text on page 272.

46 (i) Refer to text on page 271.
(ii) **Hint** $CH_3-CHI-CH_3$

47 Due to the presence of electron withdrawing group Refer to text on page 272.

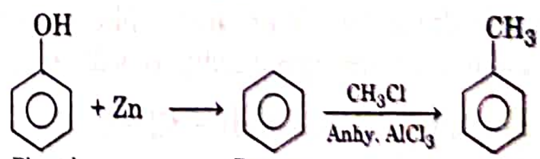
48 Refer to text on page 270.

49 Refer to text on page 273.

50 Refer to text on pages 287, 288 and 273.

51 (i) Refer to text on page 266.
(ii) (a), (b) Refer to text on pages 272 and 273.

(c)



52 (i) Refer to text on page 265 and 266.
(ii) Refer to text on page 289.

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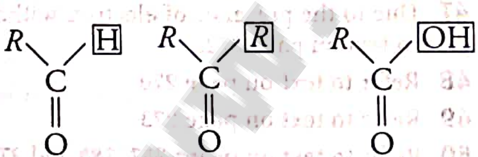
08

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

The compounds containing carbonyl group, i.e. carbon-oxygen double bond (represented as $\rangle C{=}O$) are known as **carbonyl compounds.**

Depending upon the atoms or group of atoms attached on either sides of the carbonyl group, carbonyl compounds are divided into three major classes, i.e. aldehydes, ketones and carboxylic acids.



Aldehyde Ketone Carboxylic acid

The carbonyl group is one of the most important functional groups in organic chemistry. This chapter will explore the reactivity of these functional groups. Specifically, we will see that a wide variety of nucleophiles will react with $-CHO$, $\rangle C{=}O$ and $-COOH$ groups. Many of these reactions are common in biological pathways, including the role of β-carotene in promoting healthy vision. They are responsible for many flavours and odours such as vanillin, benzaldehyde. The reactions and principles outlined in this chapter are central to the study of organic chemistry.

CHAPTER CHECKLIST

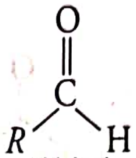
- Aldehydes and Ketones
- Carboxylic Acids

|TOPIC 1|

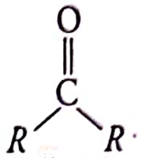
Aldehydes and Ketones

In aldehydes, the carbonyl group is bonded to a carbon and hydrogen, while in ketones, it is bonded to the two carbon atoms.

e.g.



Aldehyde



Ketone

Aldehydes and ketones are the simplest and most important carbonyl compounds.

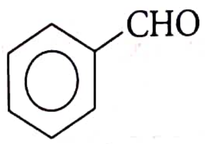
NOMENCLATURE

There are two systems of nomenclature of aldehydes and ketones. These are as follows:

Common Names

Common names of aldehydes are derived from common names of carboxylic acids (—COOH) just by replacing the ending '-ic' of carboxylic acid with aldehyde. The location of the substituent in the carbon chain is indicated by Greek letters $\alpha, \beta, \gamma, \delta$, etc. The α-carbon being the one directly linked to the $>C{=}O$ group, β- carbon the next and so on.

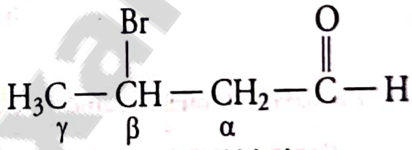
e.g.



Benzaldehyde

CH_3CHO

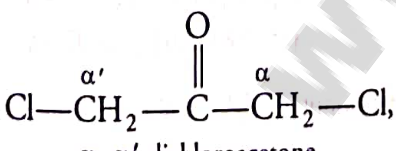
Acetaldehyde



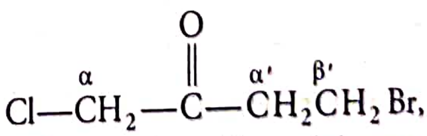
β-bromobutyraldehyde

The common names of ketones are derived by naming the two alkyl or aryl groups bonded to the carbonyl group. Alkyl phenyl ketones are usually named by adding the acyl group as prefix to phenone. The locations of substituents are indicated by Greek letters $\alpha\alpha'$, $\beta\beta'$, etc., beginning with the carbon atoms next to the carbonyl group, indicated as $\alpha\alpha'$.

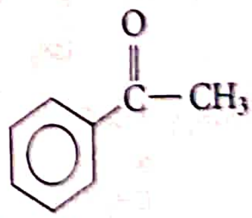
e.g.



α, α'-dichloroacetone



β'-bromoethyl-α- chloromethylketone

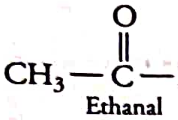


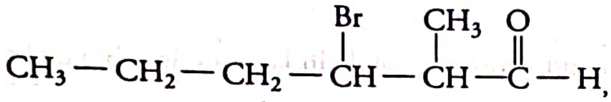
Acetophenone

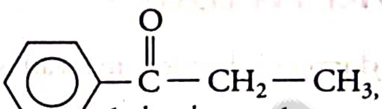
IUPAC Names

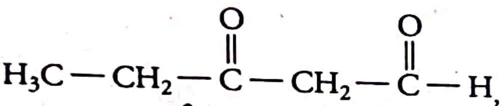
The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending 'e' with '-al' and '-one' respectively. In aldehydes, the longest carbon chain is numbered from the carbon of the aldehyde group whereas numbering starts from the end nearer to the carbonyl group in ketones. The substituents are prefixed in alphabetical order along with numerals indicating their positions in the carbon chain. The same applies to cyclic ketones, where the carbonyl carbon is numbered one. When the aldehydic group is attached to a ring, the suffix carbaldehyde is added after the full name of cycloalkane.

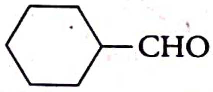
The numbering of the ring carbon atoms start from the carbon atom attached to the aldehyde group. The name of the simplest aromatic aldehyde carrying the aldehyde group on a benzene ring is benzenecarbaldehyde or benzaldehyde. However, the common name benzaldehyde is also accepted by IUPAC.

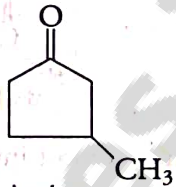

Ethanal

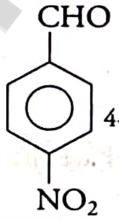

3-bromo-2-methylhexan-1-al

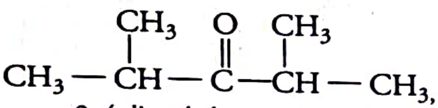

1-phenylpropan-1-one


3-oxopentanal

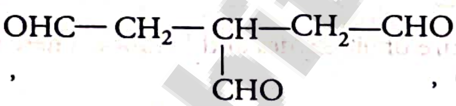

Cyclohexanecarbaldehyde

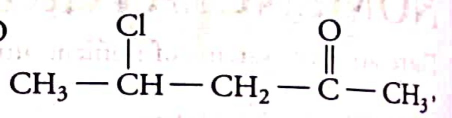

3-methylcyclopentanone

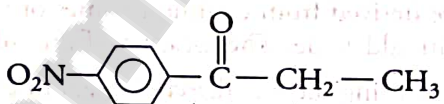

4-nitrobenzaldehyde, or 4-nitrobenzene carbaldehyde


2, 4-dimethylpentan-3-one

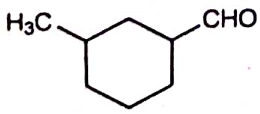

4-methylbenzaldehyde (or *p*-methylbenzaldehyde)

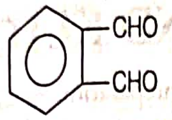
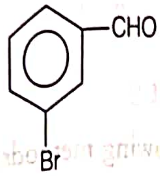
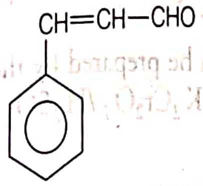
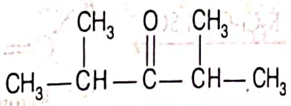
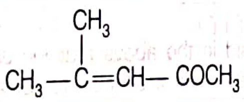
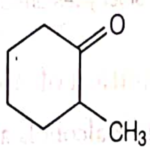

Propane-1,2,3-tricarbaldehyde


4-chloropentan-2-one


1-(*p*-nitro) phenyl propan-1-one or *p*-nitropropiophenone

Common and IUPAC names of some aldehydes and ketones

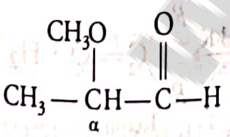
Structural formula	Common name	IUPAC name
Aldehydes		
HCHO	Formaldehyde	Methanal
$CH_3—CHO$	Acetaldehyde	Ethanal
$CH_3—CH_2—\overset{\alpha}{C}H(CH_3)—CHO$	α-methylbutyraldehyde	2-methylbutanal
$(CH_3)_2CHCHO$ or $CH_3—CH(CH_3)—CHO$	*iso* butyraldehyde	2-methylpropanal
$CH_3—CH_2—CH_2—CH_2—CHO$	Valeraldehyde	Pentanal
$CH_2=CH—CHO$	Acrolein	Prop-2-en-1-al
$CH_3—\overset{\alpha}{C}H(OCH_3)—CHO$	α-methoxypropionaldehyde	2-methoxypropanal
	γ-methylcyclohexanecarbaldehyde	3-methylcyclohexanecarbaldehyde

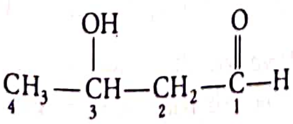
Structural formula	Common name	IUPAC name
	Phthaldehyde	Benzene-1,2-dicarbaldehyde
	*m*-bromobenzaldehyde	3-bromobenzenecarbaldehyde or 3-bromobenzaldehyde
$CH_3-CH=CH-CHO$	Crotonaldehyde	But-2-enal
	Cinnamaldehyde	3-phenylprop-2-enal
Ketones		
CH_3COCH_3	Acetone	Propanone
	Diisopropyl ketone	2, 4-dimethylpentan-3-one
	Mesityl oxide	4-methylpent-3-en-2-one
	α-methylcyclohexanone	2-methylcyclohexanone

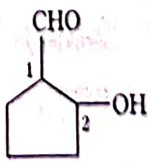
EXAMPLE |1| Draw the structures of the following compounds.

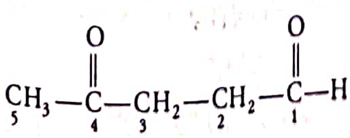
(i) α-methoxypropionaldehyde
(ii) 3-hydroxybutanal
(iii) 2-hydroxycyclopentane carbaldehyde
(iv) 4-oxopentanal
(v) Di-sec-butylketone
(vi) 4- fluoroacetophenone

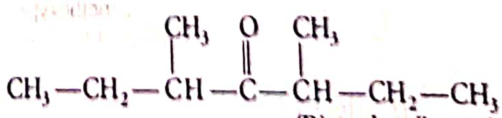
NCERT Intext

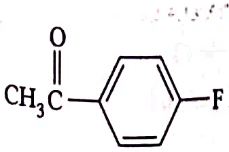
Sol. (i)  (α-methoxypropionaldehyde)

(ii)  (3-hydroxybutanal)

(iii)  (2-hydroxycyclopentane carbaldehyde)

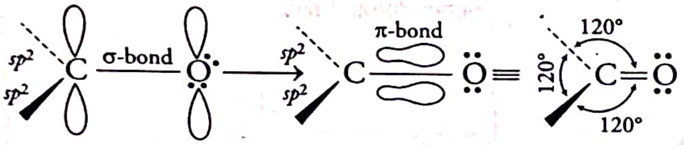
(iv)  (4-oxopentanal)

(v) 
(Di-sec-butylketone)

(vi)  (4- fluoroacetophenone)

STRUCTURE OF CARBONYL GROUP

The carbonyl carbon atom is sp^2 hybridised and forms 3 sigma (σ) bonds. The fourth valence electron of carbon remains in its p-orbital where it forms a π-bond by overlapping with p-orbital of an oxygen. The oxygen atom also have two non-bonding electron pairs. Thus, carbonyl carbon and three atoms attached to it lie in the same plane and π-electron cloud is above and below this plane.
It possesses a trigonal coplanar structure with bond angles of 120°.



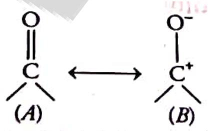
Orbital diagram for the formation of carbonyl group

Resonance of Carbonyl Group

The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen relative to carbon. As a result, the oxygen atom tends to attract the electron cloud of the π-bond towards itself due to which carbonyl-carbon acquires partial positive charge and oxygen carries a small negative charge.

Hence, the carbonyl-carbon is an electrophilic (Lewis acid) and carbonyl-oxygen a nucleophilic (Lewis base) centre. Carbonyl compounds have substantial dipole moments and are polar than ethers.

The high polarity of the carbonyl group can be explained on the basis of resonance involving a neutral (A) and dipolar (B) structures as shown below:



Resonance involving neutral (A) and dipolar (B) structures

PREPARATION OF ALDEHYDES AND KETONES

Some important methods of preparation of aldehydes and ketones are discussed below:

Preparation of Both Aldehydes and Ketones

These are prepared by the following methods:

(a) From Alcohols

By the Oxidation of Alcohols

Aldehydes and ketones can be prepared by the oxidation of alcohols with $K_2Cr_2O_7/H_2SO_4$ or $KMnO_4/KOH$.

$$\underset{1^\circ \text{ alcohol}}{RCH_2OH} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Aldehyde}}{R-CHO} + H_2O$$

$$\underset{2^\circ \text{ alcohol}}{R_2CHOH} + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\text{Ketone}}{R_2C=O} + H_2O$$

Note The aldehydes formed in the above reaction are readily oxidised to carboxylic acids if allowed to remain in the reaction mixture. Therefore, the aldehydes are distilled off as soon as they are formed.

By the Catalytic Dehydrogenation of Alcohols

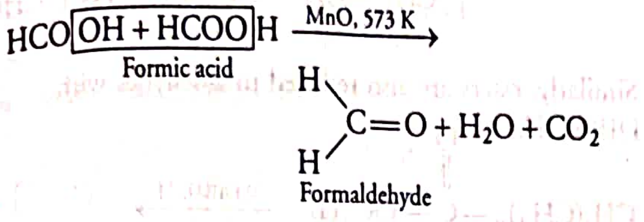
This method is suitable for volatile alcohols and has industrial application. In this method, alcohol vapours are passed over heavy metal catalysts (Ag or Cu) at 573 K.

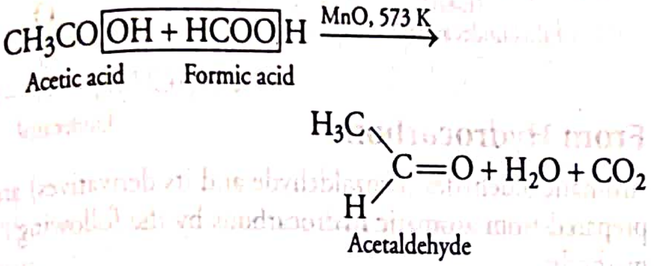
$$\underset{1^\circ \text{ alcohol}}{R-CH_2OH} \xrightarrow{Cu/573\text{ K}} \underset{\text{Aldehyde}}{R-CHO} + H_2$$

$$\underset{2^\circ \text{ alcohol}}{R_2CHOH} \xrightarrow{Cu/573\text{ K}} \underset{\text{Ketone}}{R_2C=O} + H_2$$

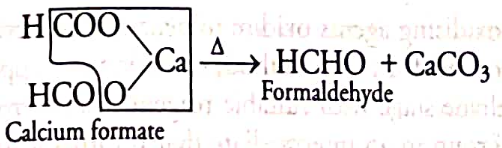
(b) From Carboxylic Acids

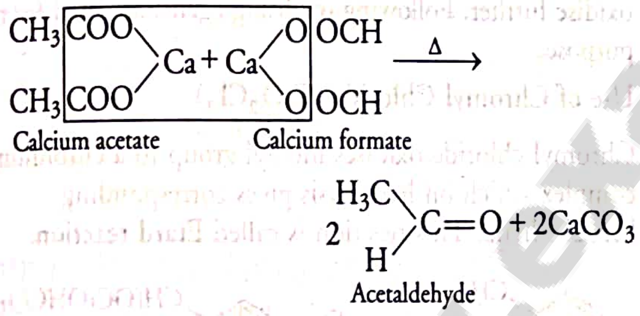
(a) By passing vapours of carboxylic acids over manganous oxide at 573 K.

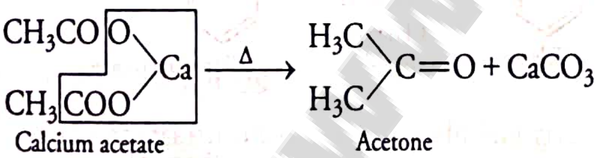




(b) By the dry distillation of calcium salt of fatty acids.





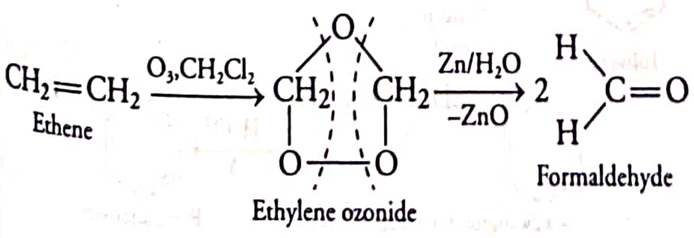


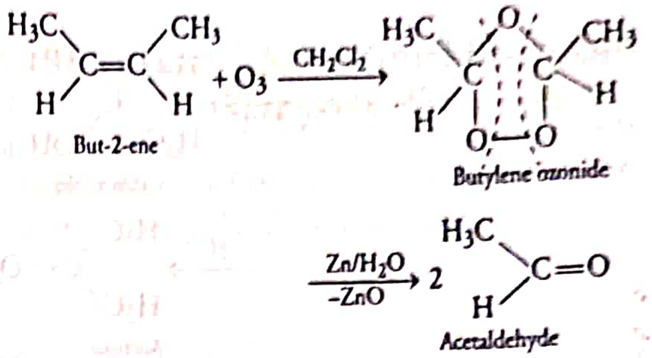
Note This method is not suitable for the preparation of aldehydes except HCHO, since the yields are low.

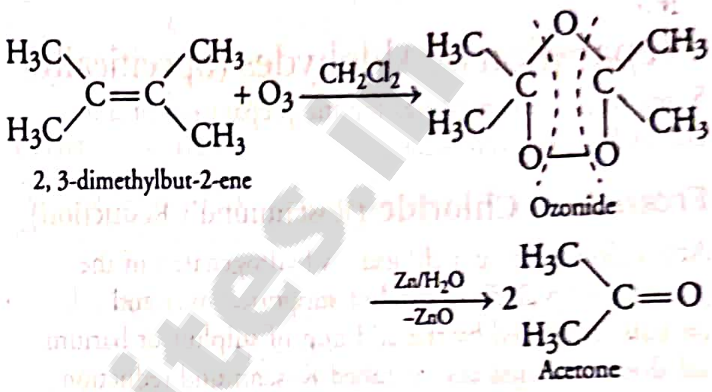
(c) From Hydrocarbons

By the Reductive Ozonolysis of Alkenes

Ozonolysis of alkenes followed by the reaction with zinc dust and water gives aldehydes, ketones or both depending on the substitution pattern of the alkene.

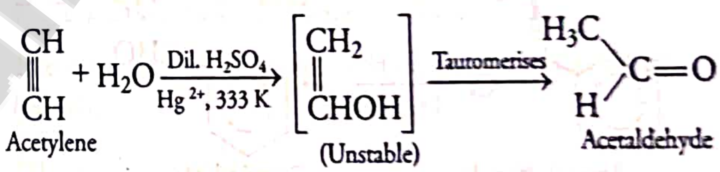


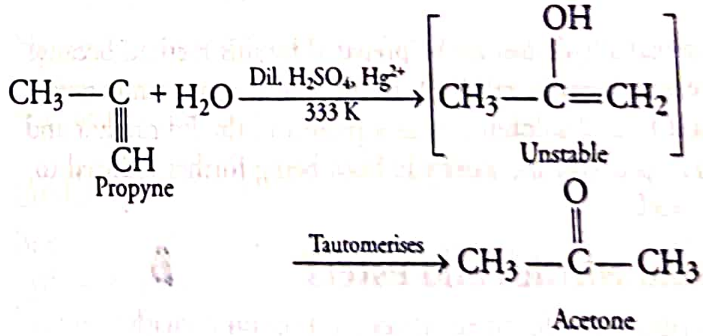




By the Hydration of Alkynes

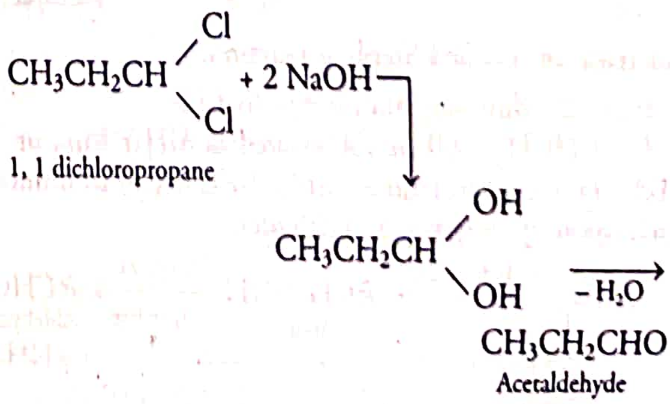
Addition of water to ethyne in the presence of dil. H_2SO_4 and $HgSO_4$ gives acetaldehyde. All other alkynes give ketones in the reaction.

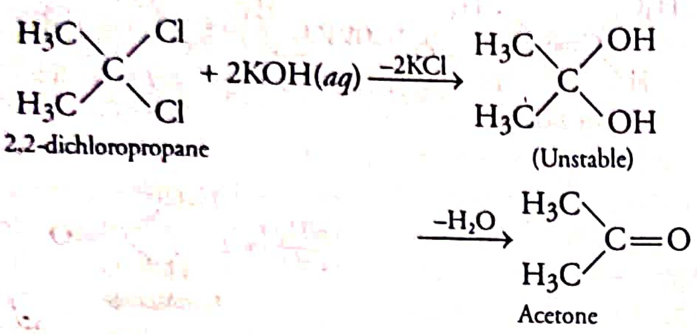




From *gem*-Dihalides

By the hydrolysis of *gem*-dihalides in aqueous KOH, aldehyde and ketones are obtained.





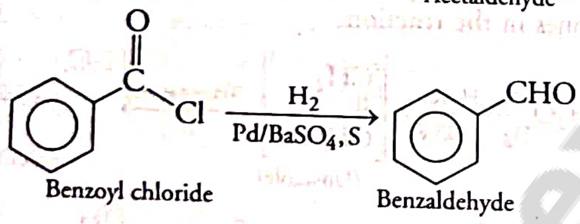
Preparation of Aldehydes (Specifically)

Some important methods for the preparation of only aldehydes are given below:

From Acyl Chloride (Rosenmund's Reduction)

Acyl chloride or acid chloride is hydrogenated in the presence of palladium catalyst supported over and partially poisoned by the addition of sulphur or barium sulphate. This reaction is called Rosenmund reduction.

$$\underset{\text{Acetyl chloride}}{CH_3-\overset{O}{\overset{\|}{C}}-Cl} \xrightarrow[Pd/BaSO_4,\ S]{H_2} \underset{\text{Acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H}$$



Formaldehyde cannot be prepared by this method because formyl chloride, HCOCl is unstable at room temperature. $BaSO_4$ and sulphur acts as a poison to the Pd catalyst and thus, prevents the aldehyde from being further reduced to alcohols.

From Nitriles and Esters

Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.

$$\underset{\text{Nitrile}}{RCN} + SnCl_2 + HCl \longrightarrow \underset{\text{Imine}}{RCH{=}NH} \xrightarrow{H_3O^+} \underset{\text{Aldehyde}}{RCHO}$$

This reaction is called **Stephen reaction.**

Alternatively, diisobutylaluminium hydride, $[(CH_3)_2CHCH_2]_2AlH$ is abbreviated as $AlH(i\text{-Bu})_2$ or DIBAL-H is used to reduce nitriles (selectively) to imines which upon hydrolysis give aldehydes.

$$RCN \xrightarrow{(i)\ AlH(i\text{-Bu})_2} \underset{\text{Imine}}{RCH{=}NH} \xrightarrow[\text{Hydrolysis}]{(ii)\ H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_3$$

$$\underset{\text{Hex-4-en-1-nitrile}}{CH_3-CH{=}CH-CH_2CH_2CN} \xrightarrow[(ii)\ H_2O]{(i)\ AlH(i\text{-Bu})_2} \underset{\text{Hex-4-en-1-al}}{CH_3-CH{=}CH-CH_2CH_2-CHO}$$

Similarly, esters are also reduced to aldehydes with DIBAL-H.

$$\underset{\text{Ethyl undecanoate}}{CH_3(CH_2)_9-\underset{\text{(Ester)}}{\overset{O}{\overset{\|}{C}}}-OC_2H_5} \xrightarrow[(ii)\ H_2O]{(i)\ DIBAL\text{-}H} \underset{\text{Undecanal}}{CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-H}$$

From Hydrocarbons

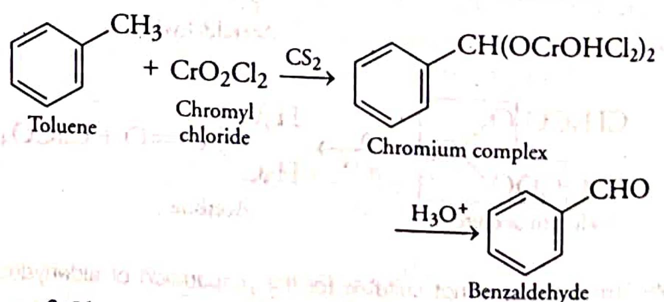
Aromatic aldehydes (benzaldehyde and its derivatives) are prepared from aromatic hydrocarbons by the following methods:

By the Oxidation of Methylbenzene

Strong oxidising agents oxidise toluene and its derivatives to benzoic acid. In this method, oxidation is stopped at the aldehyde stage with suitable reagents that converts the methyl group to an intermediate that is difficult to oxidise further. Following oxidising agents are used for this purpose.

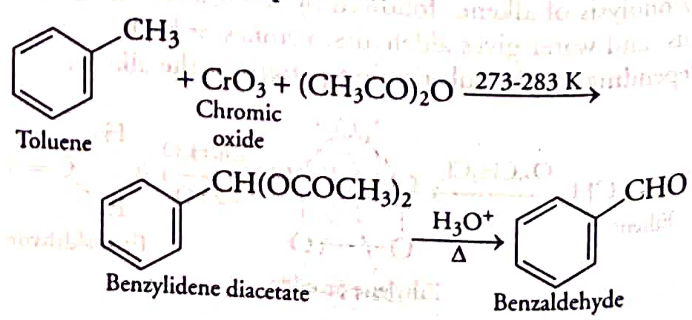
Use of Chromyl Chloride (CrO_2Cl_2)

Chromyl chloride oxidises methyl group to a chromium complex which on hydrolysis gives corresponding benzaldehyde. This reaction is called **Etard reaction.**



Use of Chromic Oxide (CrO_3)

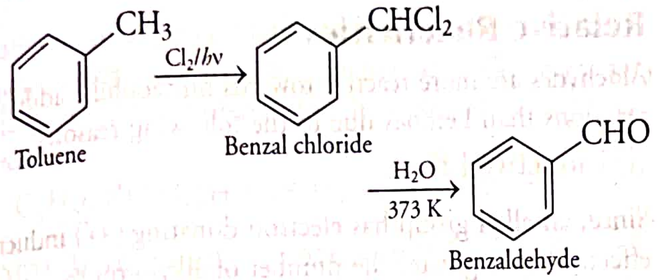
Toluene or substituted toluene on treatment with CrO_3 in acetic anhydride, gets converted to benzylidene diacetate. The reaction can be depicted as:



By Side Chain Chlorination followed by Hydrolysis

Toluene on chlorination gives benzal chloride, which on hydrolysis gives benzaldehyde. This reaction is a commercial method for the manufacture of benzaldehyde.

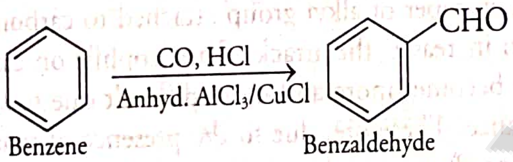
The reaction can be depicted as:



This is a commercial method for the manufacture of benzaldehyde.

By Gattermann-Koch Reaction

When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde. This reaction is known as Gattermann-Koch reaction.



Preparation of Ketones (Specifically)

Some important methods for the preparation of ketones are given below:

From Acyl Chlorides

Acyl chlorides, on treatment with dialkylcadmium gives ketones.

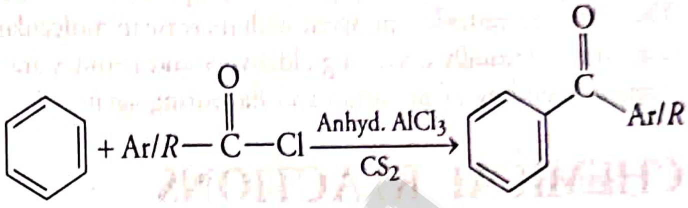
$$\underset{\text{Grignard reagent}}{2R\text{—Mg—}X} + CdCl_2 \xrightarrow{\text{Dry ether}} \underset{\text{Dialkyl cadmium}}{R_2Cd} + 2Mg(X)Cl$$

$$2R'\text{—}\underset{\underset{O}{\|}}{C}\text{—Cl} + \underset{\text{Dialkyl cadmium}}{R_2Cd} \xrightarrow{\text{Dry ether}} 2R'\text{—}\underset{\underset{O}{\|}}{C}\text{—}R + CdCl_2$$

$$\text{e.g. } \underset{\text{Acetyl chloride}}{2CH_3\text{—}\overset{\overset{O}{\|}}{C}\text{—Cl}} + \underset{\text{Diethyl cadmium}}{(CH_3CH_2)_2Cd} \xrightarrow{\text{Dry ether}} \underset{\text{Butanone}}{2CH_3\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_2CH_3} + CdCl_2$$

From Benzene or Substituted Benzene

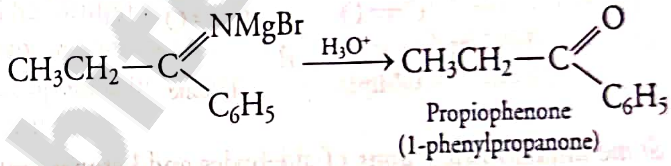
When benzene or substituted benzene is treated with acid chloride in the presence of anhydrous aluminium chloride, a corresponding ketone is obtained. This reaction is known as Friedel-Crafts acylation reaction.



From Nitriles

When a nitrile is treated with Grignard reagent followed by hydrolysis yields a ketone.

$$C_6H_5MgBr + CH_3\text{—}CH_2C{\equiv}N \xrightarrow{\text{Ether}}$$



PHYSICAL PROPERTIES

The physical properties of aldehydes and ketones are as follows:

Physical State

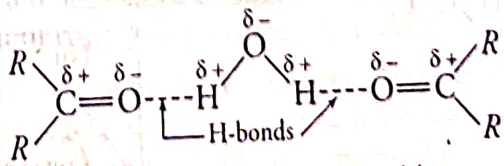
Methanal is a gas at room temperature. Ethanal is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature.

Boiling Points

Boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses because weak intermolecular association arises due to dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to the absence of intermolecular hydrogen bonding.

Solubility

Lower members of aldehydes and ketones like methanal, ethanal and propanone are miscible with water in all proportions because they form hydrogen bond with water.



However, the solubility of aldehydes and ketones decreases when the length of alkyl chain increases.

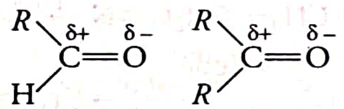
All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc.

Odour

Lower aldehydes have sharp pungent (unpleasant) odours. The odour becomes less pungent with increase in molecular size. Many naturally occurring aldehydes and ketones are used in blending of perfumes and flavouring agents.

CHEMICAL REACTIONS

Aldehydes and ketones are highly reactive compounds. Since, both of these possess the same functional group, i.e. polarised carbonyl group, they undergo a number of common reactions.



Aldehyde Ketone

Some important reactions of aldehydes and ketones are as follows:

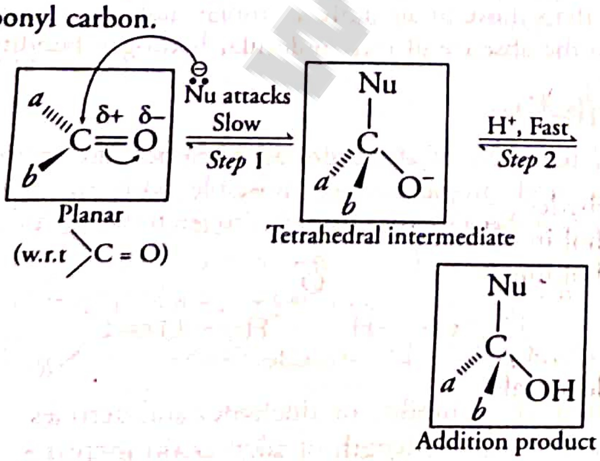
Nucleophilic Addition Reactions

Both alkenes and carbonyl compounds, i.e. aldehydes and ketones are unsaturated compounds. However, unlike alkenes which undergo electrophilic addition reactions, aldehydes and ketones undergo nucleophilic addition reactions.

Mechanism

Carbonyl group being polar (due to greater electronegativity of oxygen as compared to carbon), behaves as an electrophile in the presence of nucleophile.

Thus, the nucleophile readily attacks the electrophilic carbon atom of carbonyl group in the direction perpendicular to the plane of sp^2-hybridised orbitals of carbonyl carbon.



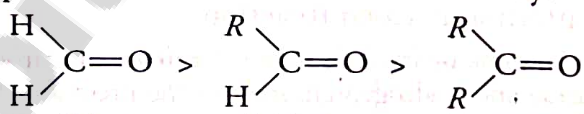
The hybridisation of carbon changes from sp^2 to sp^3 in this process and tetrahedral alkoxide intermediate is formed. The intermediate then picks up a proton either from the solvent (usually H_2O) or from the reagent to give electrically neutral addition product. The net result is addition of Nu^- and H^+ across the carbon oxygen double bond.

Relative Reactivities

Aldehydes are more reactive towards nucleophilic addition reactions than ketones due to the following reasons:

(i) Inductive Effect

Since, an alkyl group has electron donating ($+I$) inductive effect. Hence, greater the number of alkyl groups attached to carbonyl group, greater the electron density on carbonyl carbon. Thus, it lowers the attack of nucleophile that results in a decrease in reactivity.

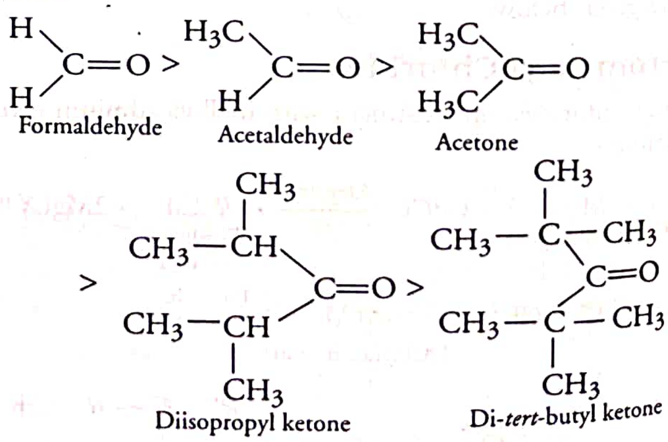


Formaldehyde Aldehyde Ketone

(ii) Steric Effect

As the number of alkyl group attached to carbonyl carbon increases, the attack of nucleophile on carbonyl group becomes more and more difficult due to steric hindrance. Therefore, due to the presence of two bulky alkyl (or R) groups, the attack of nucleophile is hindered and hence, ketones are less reactive than aldehydes.

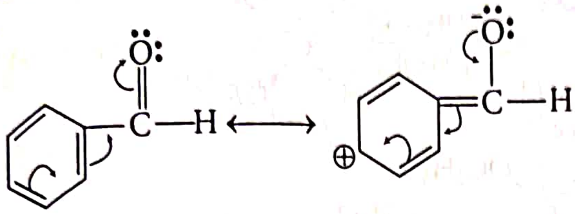
Thus, the reactivity of the following carbonyl compounds decreases :



Reactivity of Aromatic Aldehydes and Ketones

In general, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic analogues because electron donating resonance effect ($+R$-effect) of the benzene ring increases the electron density on the carbonyl carbon.

This makes the carbonyl carbon less electrophilic.



However, amongst aromatic aldehydes and ketones, aromatic aldehydes are more reactive than alkyl aryl ketones which in turn are more reactive than diaryl ketones.

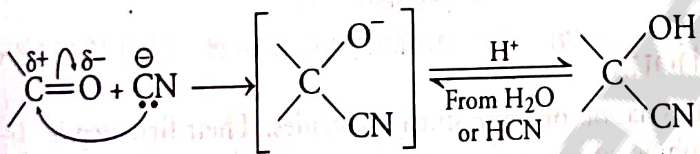
$$C_6H_5CHO > C_6H_5COCH_3 > C_6H_5COC_6H_5$$

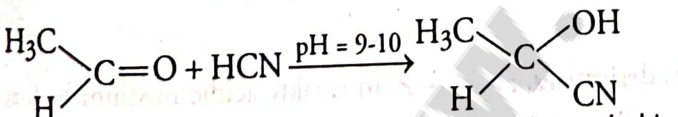
Some Important Examples of Nucleophilic Addition Reactions

Addition of Hydrogen Cyanide (HCN)

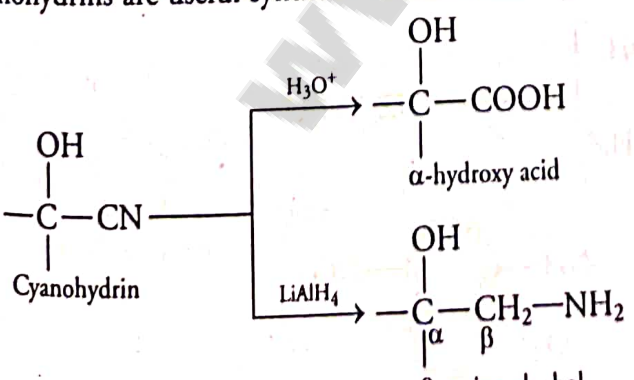
Aldehydes and ketones on reaction with HCN give cyanohydrins. This reaction is very slow with pure HCN. So, it is catalysed by a base and the generated CN^- being a stronger nucleophile readily attacks on carbonyl-carbon to yield corresponding cyanohydrin.

$$HO^{-} + H-CN \rightleftharpoons :\bar{C}N + H_2O$$



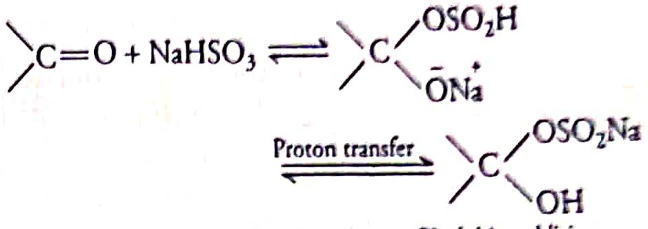


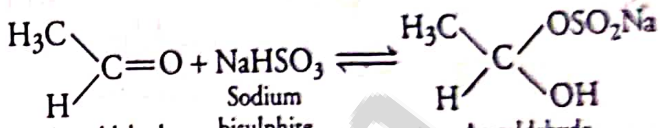
Cyanohydrins are useful synthetic intermediate. e.g.



Addition of Sodium Hydrogen Sulphite ($NaHSO_3$)

Most of the aldehydes and aliphatic methyl ketones which are not sterically hindered, on reaction with $NaHSO_3$ give bisulphite addition product.





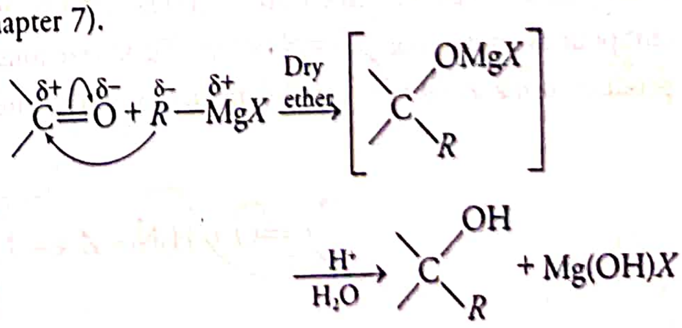
The position of the equilibrium lies largely to the right hand side for most aldehydes and to the left for most ketones due to steric reasons.

The bisulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali.

Therefore, these are useful for separation and purification of aldehydes.

Addition of Grignard Reagents

Aldehydes and ketones on reaction with Grignard reagent give addition products which upon hydrolysis with water or dilute mineral acids give alcohols. The type of alcohol formed depends upon the aldehyde or ketone used (formaldehyde $\rightarrow$ 1° alcohols, other aldehydes $\rightarrow$ 2° alcohols and ketones $\rightarrow$ 3° alcohols, discussed in chapter 7).

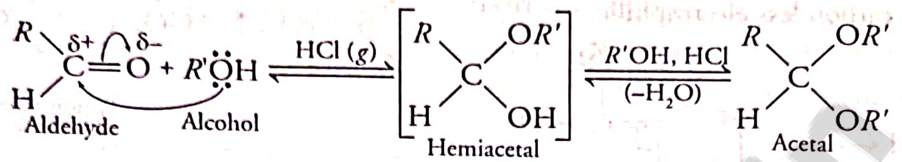


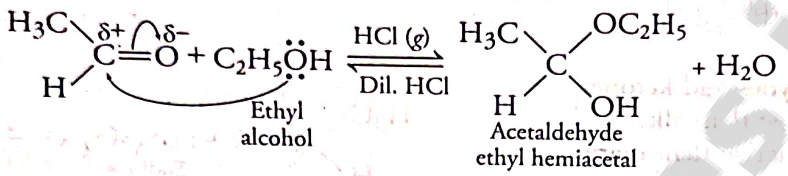
Addition of Alcohols

Aldehydes react with one equivalent of a monohydric alcohol in the presence of dry HCl gas to yield alkoxy alcohol intermediate known as **hemiacetals**.

Hemiacetals on further reaction with one more molecule of alcohol give acetals. (Hemiacetals are alkoxy alcohols while acetals are *gem*-dialkoxy compounds).

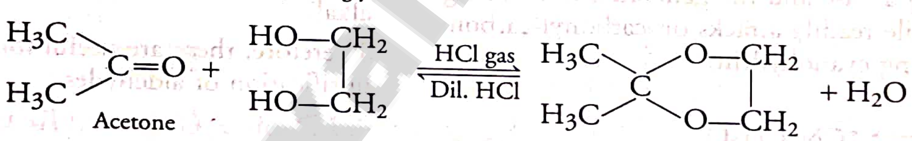
e.g.





In this reaction, dry HCl gas protonates the oxygen atom of the carbonyl compound, thereby increasing the electrophilicity of the carbonyl carbon and hence facilitating the nucleophilic attack by the alcohol molecule. Ketones, however, do not react with monohydric alcohols but they react with dihydric alcohol such as ethylene glycol to give cyclic ketals.

e.g.



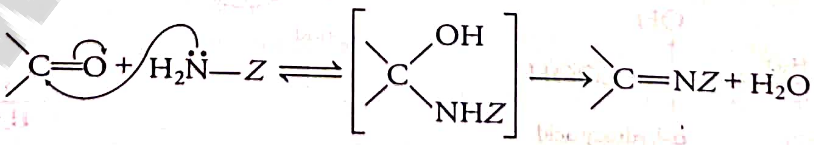
Note Acetals and ketals are hydrolysed by dilute acids and generate original aldehydes and ketones respectively.

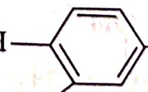
Nucleophilic Addition Elimination Reactions

These are two step reactions involving addition followed by elimination of some small molecules. Their first step is similar to nucleophilic addition reactions. Examples of nucleophilic addition elimination reaction are as follows:

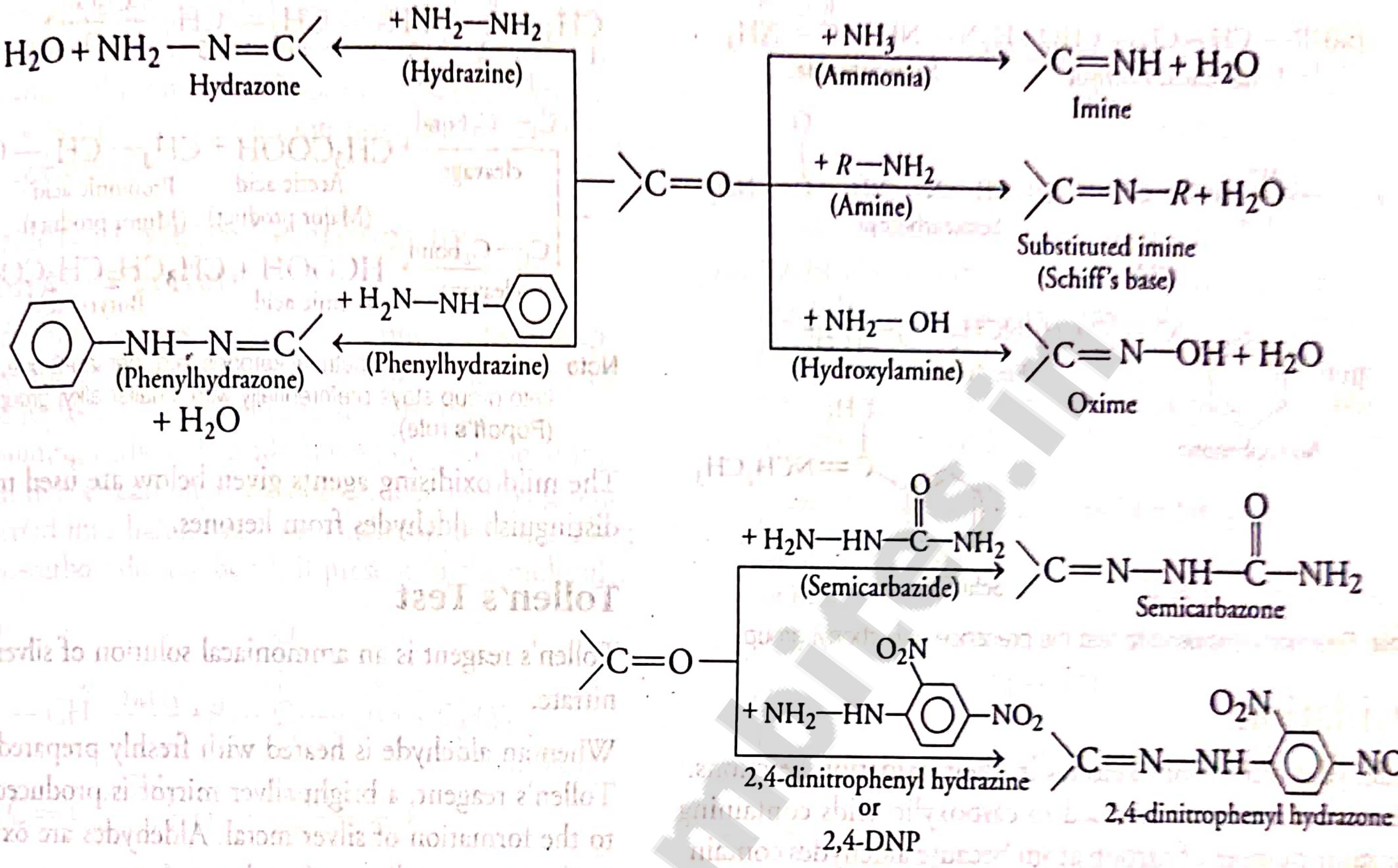
Addition of Ammonia and its Derivatives

Aldehydes and ketones react with ammonia and a number of its derivatives, $H_2N—Z$ in weakly acidic medium to form compounds containing $>C=N$ group. These reactions are reversible and catalysed by acid. The equilibrium favours the product formation due to rapid dehydration of the intermediate to form $>C=N—Z$ type compounds.



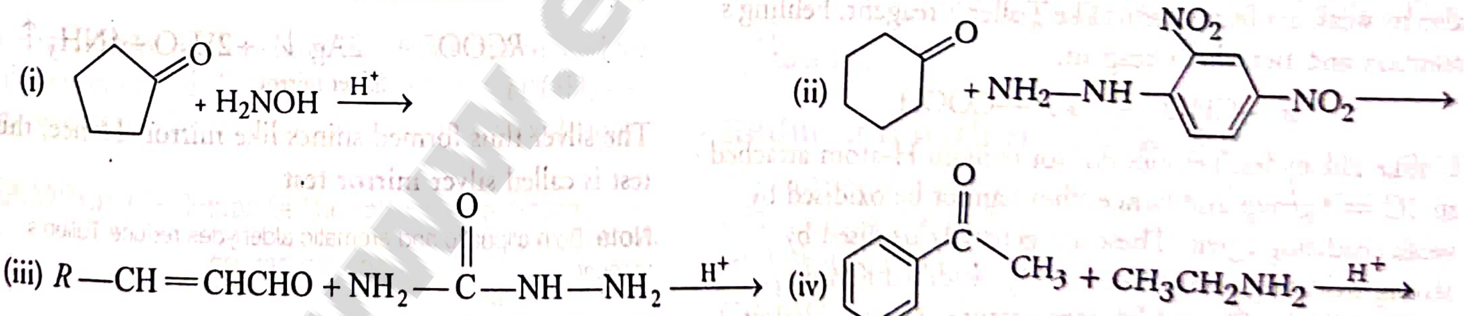
(where, Z = H, alkyl, aryl, — OH, — NH_2, — $NHCONH_2$ and —NH——NO_2)

The reactions of carbonyl group with substituted N-derivatives can be summarised as:



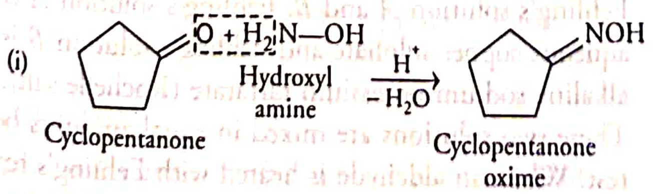
Note 2,4-dinitrophenyl hydrazine is **Brady's reagent**. Aldehydes and ketones react with it to form yellow, orange or red ppt. of 2,4-dinitrophenyl hydrazone. These are useful for the characterisation of aldehydes and ketones.

EXAMPLE |2| Predict the products of the following reactions:

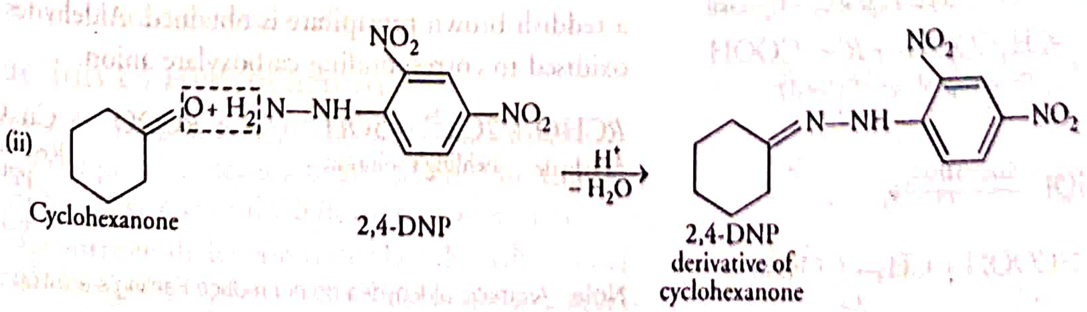


Elimination of H_2O from carbonyl and amine group and formation of $C=N$ bond.

Sol. (i)



(ii)



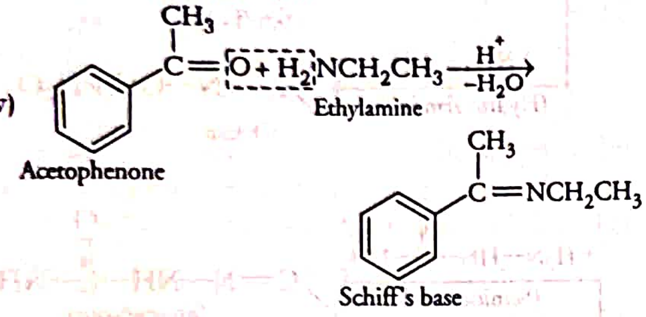
(iii) $R—CH{=}CH—CHO + H_2N—NH—\overset{\overset{\displaystyle O}{\|}}{C}—NH_2$

Unsaturated aldehyde Semicarbazide

$\xrightarrow[-H_2O]{H^+} R—CH{=}CH—CH{=}N—NH—\overset{\overset{\displaystyle O}{\|}}{C}—NH_2$

Semicarbazone

(iv)



Note Reaction (ii) is used to test the presence of carbonyl group.

Oxidation

Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids containing the same number of carbon atom because aldehydes contain H-atom attached to carbonyl group, which can be converted into —OH group without involving the cleavage of any other bond. Thus, they are oxidised not only by strong oxidising agents like HNO_3, $KMnO_4$ and $K_2Cr_2O_7$ but also by weak oxidising agents like Tollen's reagent, Fehling's solution and Benedict's reagent.

$$R—CHO \xrightarrow{[O]} R—COOH$$

Unlike aldehydes, ketones do not contain H-atom attached to $\rangle C{=}O$ group and hence, they cannot be oxidised by weak oxidising agent. These are generally oxidised by strong oxidising agents like HNO_3, acidified $KMnO_4$, acidified $K_2Cr_2O_7$ at high temperature. Their oxidation involves carbon-carbon bond cleavage with the formation of a mixture of carboxylic acids each containing lesser number of carbon atoms than the original ketone.

$$R—\overset{1}{C}H_2—\underset{\underset{\displaystyle O}{\|}}{\overset{2}{C}}—\overset{3}{C}H_2—R' \xrightarrow{[O]} R—COOH + R'—CH_2COOH$$

(By cleavage of $C_1—C_2$ bond)

Or $R—CH_2COOH + R'—COOH$

(By cleavage of $C_2—C_3$ bond)

$$\underset{(3\,C)}{CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3} + 3[O] \xrightarrow{\text{Conc. } HNO_3} \underset{(1C)}{HCOOH} + \underset{(2C)}{CH_3—COOH}$$

$$\underset{\text{Pentan-2-one}}{\overset{1}{C}H_3—\underset{2}{\overset{\overset{\displaystyle O}{\|}}{C}}—\overset{3}{C}H_2—\overset{4}{C}H_2—\overset{5}{C}H_3} \xrightarrow[H_2SO_4]{K_2Cr_2O_7}$$

$\xrightarrow[\text{cleavage}]{C_2—C_3 \text{ bond}}$ $\underset{\substack{\text{Acetic acid}\\\text{(Major product)}}}{CH_3COOH} + \underset{\substack{\text{Propionic acid}\\\text{(Minor product)}}}{CH_3—CH_2—COOH}$

$\xrightarrow[\text{cleavage}]{C_1—C_2 \text{ bond}}$ $\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Butyric acid}}{CH_3CH_2CH_2COOH}$

Note In case of unsymmetrical ketones, e.g. pentan-2-one, the keto group stays preferentially with smaller alkyl group **(Popoff's rule).**

The mild oxidising agents given below are used to distinguish aldehydes from ketones.

Tollen's Test

Tollen's reagent is an ammoniacal solution of silver nitrate.

When an aldehyde is heated with freshly prepared Tollen's reagent, a bright silver mirror is produced due to the formation of silver metal. Aldehydes are oxidised to the corresponding carboxylate anion.

The reaction occurs in alkaline medium.

$$\underset{\text{Aldehyde}}{RCHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \xrightarrow{\Delta} RCOO^- + \underset{\text{Silver mirror}}{2Ag\downarrow} + 2H_2O + 4NH_3\uparrow$$

The silver thus formed shines like mirror. Hence, this test is called **silver mirror test.**

Note Both aliphatic and aromatic aldehydes reduce Tollen's reagent.

Fehling's Test

Fehling's reagent is a mixture of two solutions, i.e. Fehling's solution *A* and *B*. Fehling's solution *A* is an aqueous copper sulphate and Fehling's solution *B* is an alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. When an aldehyde is heated with Fehling's reagent, a reddish-brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion.

$$\underset{\text{Aldehyde}}{RCHO} + \underset{\text{Fehling's solution}}{2Cu^{2+} + 5OH^-} \xrightarrow{\Delta} RCOO^- + \underset{\substack{\text{Red-brown}\\\text{ppt.}}}{Cu_2O\downarrow} + 3H_2O$$

Note Aromatic aldehydes do not reduce Fehling's solution.

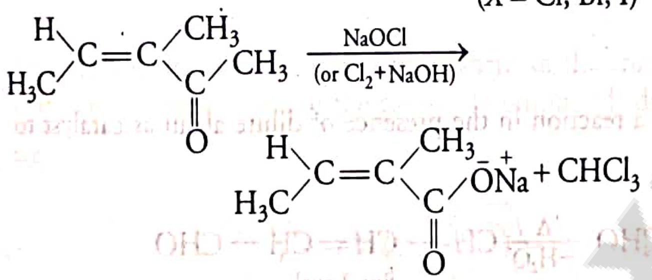
Benedict's Test

Benedict's solution is an alkaline solution of Cu^{2+} ions complexed with citrate ions. (whereas, Fehling's solution is an alkaline solution of Cu^{2+} ions complexed with tartarate ions.) Benedict's solution reacts in the same way as Fehling's solution.

Oxidation of Methyl Ketones by Haloform Reaction

Aldehydes and ketones having atleast one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted into haloform. This oxidation does not affect a carbon-carbon double bond, if present in the molecule.

$$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{NaOX} R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{Na} + CHX_3$$
$(X = Cl, Br, I)$



Iodoform reaction with sodium hypoiodite is also used for the detection of CH_3CO- group or $CH_3CH(OH)-$ group which produces CH_3CO- group on oxidation.

EXAMPLE |3| Complete the following reaction:

$$CH_3CH_2CH_2COCH_3 \xrightarrow[H^+/H_2O]{I_2/NaOH} ?$$

Sol. $\underset{\text{Pentan-2-one}}{CH_3CH_2CH_2COCH_3} \xrightarrow[H^+/H_2O]{I_2/NaOH} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH} + \underset{\text{Iodoform}}{CHI_3} \downarrow$

Reduction

Aldehydes and ketones can be reduced to a variety of compounds under different conditions.

Reduction to Hydrocarbons

The carbonyl group of an aldehyde or ketone is reduced to methylene group to form a hydrocarbon. This can be achieved by either one of the following two reactions:

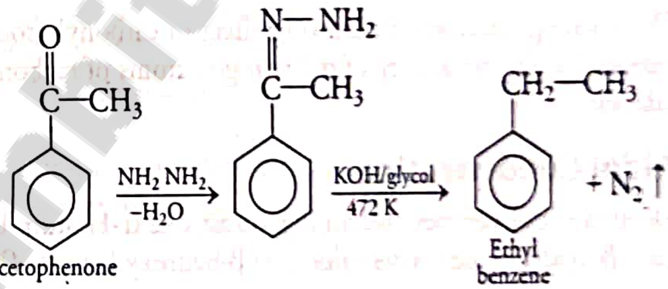
(a) **Clemmensen Reduction** It involves the reduction of carbonyl group ($\rangle C=O$) to $\rangle CH_2$ group and it is carried out in the presence of Zn amalgam and conc. HCl.

$$\rangle C=O + 4[H] \xrightarrow{\text{Zn-Hg/Conc. HCl}} \underset{\text{Hydrocarbon}}{\rangle CH_2} + H_2O$$

It is widely used for the reduction of aldehydes and ketones which are sensitive to alkalies.

(b) **Wolff-Kishner Reduction** In this method, the aldehyde or ketone is heated with hydrazine and KOH or NaOH in high boiling solvent such as ethylene glycol. It is used when carbonyl compounds are sensitive to acids.

$$\underset{\text{Aldehyde or Ketone}}{\rangle C=O} \xrightarrow[-H_2O]{+NH_2-NH_2} \rangle C=N-NH_2 \xrightarrow[\text{Ethylene glycol}]{KOH/\Delta} \rangle CH_2 + N_2\uparrow$$



$$\underset{\text{Acetaldehyde}}{\overset{H_3C}{\underset{H}{\rangle}}C=O} \xrightarrow[\text{(ii) KOH + glycol, 473 K}]{\text{(i) } NH_2NH_2} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O + N_2\uparrow$$

Reduction with HI and Red P

Aldehydes and ketones on heating with HI (hydroiodic acid) and red P at 423 K are reduced to their corresponding alkanes.

$$CH_3CHO + 4HI \xrightarrow{\text{Red P, 423 K}} CH_3-CH_3 + H_2O + 2I_2$$

$$CH_3COCH_3 + 4HI \xrightarrow[\text{423 K}]{\text{Red P}} CH_3CH_2CH_3 + H_2O + 2I_2$$

Reduction to Alcohols

Aldehydes and ketones are reduced to 1° and 2° alcohols, respectively. It is carried out either catalytically (H_2 + Ni /Pt /Pd) or chemically ($LiAlH_4$ or $NaBH_4$).

$$\underset{\text{Aldehyde}}{R-CHO} + 2[H] \xrightarrow[\text{or } NaBH_4]{LiAlH_4} \underset{\text{1°alcohol}}{R-CH_2-OH}$$

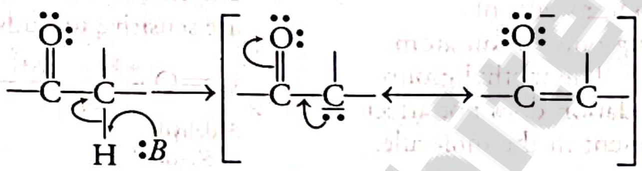
$$\underset{\text{Ketone}}{\overset{R}{\underset{R'}{\rangle}}C=O} + H_2 \xrightarrow{\text{Ni or Pt}} \underset{\text{2°alcohol}}{\overset{R}{\underset{R'}{\rangle}}CH-OH}$$

Reactions due to α-Hydrogen

The aldehydes and ketones undergo a number of reactions due to the acidic nature of α-H which in turn is due to the strong electron withdrawing effect of $>C{=}O$ group.

Acidity of α-Hydrogens of Aldehydes and Ketones

The carbon atom next to carbonyl group is called **α-carbon atom** and hydrogens attached to α-carbon atom are called **α-hydrogens**. Due to strong electron withdrawing effect of carbonyl group, the α-carbon atom becomes electron deficient, which in turn, withdraws electrons from C_α—H bond. As a result, the electron density in C_α—H bond decreases and hence, α-H atom becomes weakly held which can be easily abstracted by strong bases forming enolate ion which are stabilised by resonance as given below:



Resonance stabilised enolate anion

Thus, strong electron withdrawing effect of carbonyl group and resonance stabilisation of the conjugate base are responsible for the acidity of α-hydrogen atoms of carbonyl compounds. The reactions due to α-hydrogens are as follows:

Aldol Condensation

Aldehydes and ketones containing atleast one α-H atom undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (Ketol).

$$\underset{\text{Ethanal}}{2CH_3-CHO} \xrightleftharpoons{\text{Dil. NaOH}} \underset{\substack{\text{3-hydroxybutanal}\\\text{(Aldol)}}}{CH_3-\underset{\substack{|\\OH}}{CH}-CH_2-CHO} \xrightarrow[-H_2O]{\Delta} \underset{\substack{\text{But-2-enal}\\\text{(Aldol condensation product)}}}{CH_3-CH{=}CH-CHO}$$

$$\underset{\text{Propanone}}{2CH_3-CO-CH_3} \xrightleftharpoons{Ba(OH)_2} \underset{\substack{\text{(Ketol)}\\\text{4-hydroxy-4-methylpentan-2-one}}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2CO-CH_3} \xrightarrow[-H_2O]{\Delta} \underset{\substack{\text{4-methylpent-3-en-2-one}\\\text{(Aldol condensation}\\\text{product)}}}{CH_3-\overset{\overset{CH_3}{|}}{C}{=}CHCO-CH_3}$$

β-hydroxy aldehydes are called aldols while β-hydroxy ketones are collectively called ketols and the reaction is called **aldol condensation.** The name aldol (or ketol) is derived from the names of the two functional groups, aldehyde (or ketone) and alcohol present in the product. Aldols readily lose water to give α, β-unsaturated carbonyl compounds which are aldol condensation products. Though, ketones give ketol compounds containing a keto group and alcoholic group, yet the name aldol is used for the condensation products of two molecules of ketones due to their similarity with aldehydes.

Note Formaldehyde (HCHO), benzaldehyde (C_6H_5CHO) and benzophenone ($C_6H_5COC_6H_5$) do not undergo aldol condensation as they do not contain α-H atoms.

Cross Aldol Condensation

When aldol condensation is carried out between the two different aldehydes or ketones then reaction is said to be cross aldol condensation.

If both the reactants contain α-hydrogen atoms, the reaction gives a mixture of four products due to self condensation and cross-condensation.

$$CH_3CHO + CH_3CH_2CHO \xrightarrow[\text{(ii) }\Delta]{\text{(i) NaOH}} \underset{\substack{\text{But-2-enal}\\\text{(From two molecules}\\\text{of ethanal)}}}{CH_3-CH=CH-CHO} + \underset{\substack{\text{2-methylpent-2-enal}\\\text{(From two molecules of propanal)}}}{CH_3CH_2-CH=\underset{|\\ CH_3}{C}-CHO}$$

Simple or self aldol products

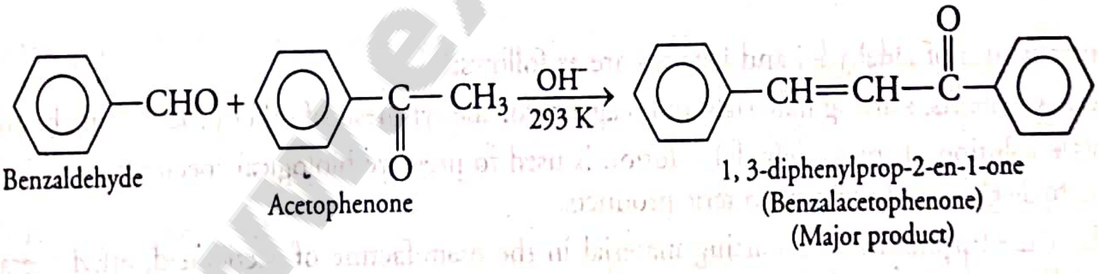
$$+ \underset{\text{2-methylbut-2-enal}}{CH_3-CH=\overset{CH_3\\|}{C}-CHO} + \underset{\text{Pent-2-enal}}{CH_3CH_2-CH=CHCHO}$$

(From one molecule of ethanal and one molecule of propanal)

Cross aldol products

Ketones can also be used as one component in the cross aldol reactions. Cross aldol condensation reactions are of great synthetic use even if one of the carbonyl compounds does not possess α-H atoms.

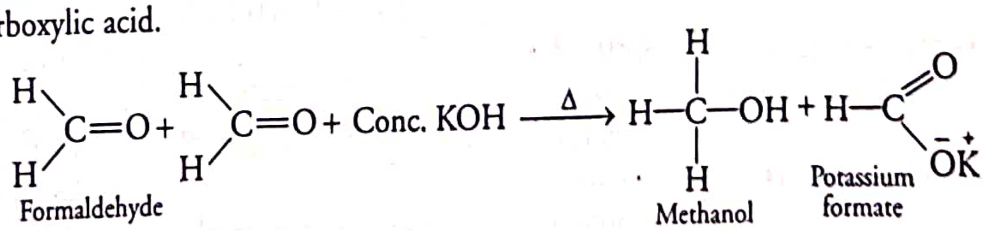
e.g.

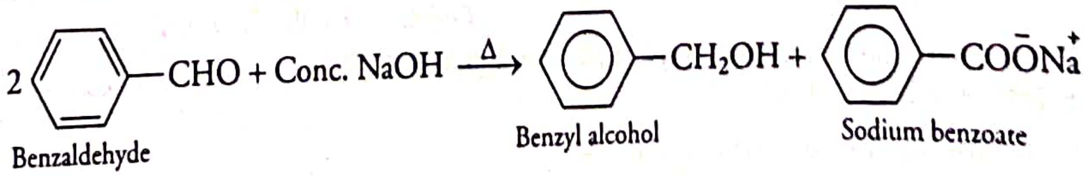


Other Reactions

Cannizzaro Reaction

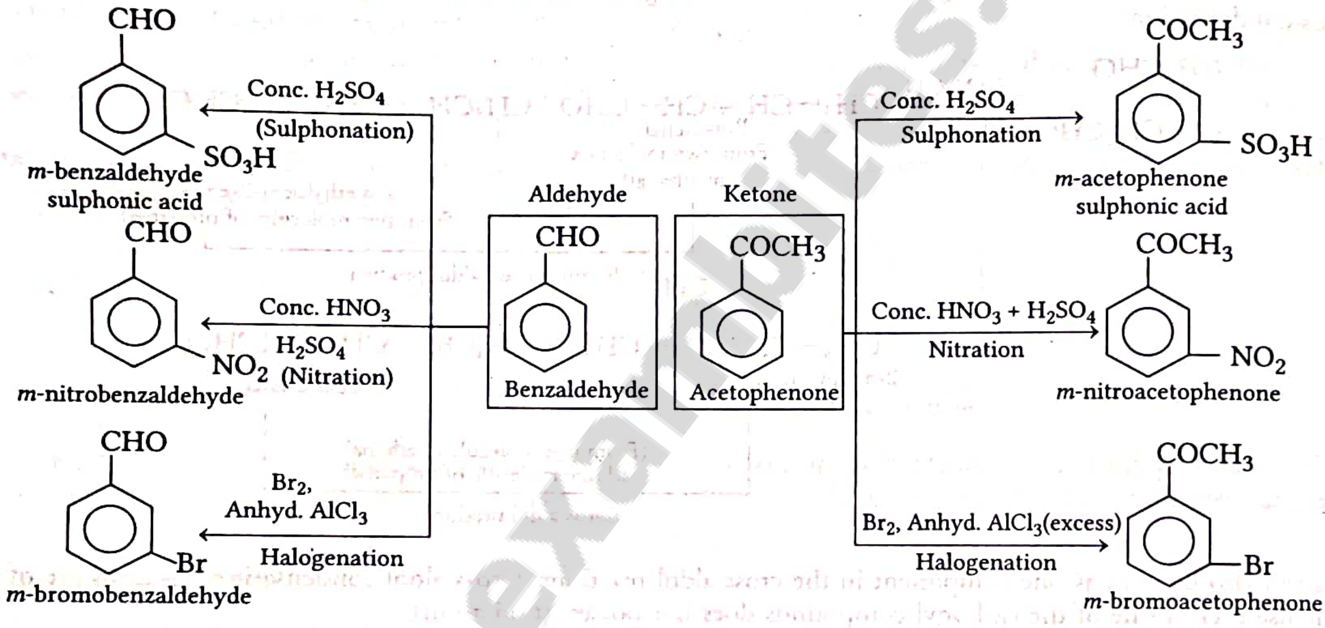
Aldehydes which do not have α-H atom undergo self oxidation and reduction (disproportionation) reactions on heating with conc. alkali. In this reaction, one molecule of aldehyde is reduced to alcohol while another molecule is oxidised to salt of carboxylic acid.





Electrophilic Substitution Reactions

Aromatic aldehydes and ketones undergo usual electrophilic substitution reactions of the benzene nucleus such as halogenation, nitration and sulphonation. Since, the aldehydic group and ketonic group are electron withdrawing groups, so they act as deactivating and *meta*-directing groups.



Uses

Some of the important uses of aldehydes and ketones are as follows:

(i) They are used as solvents, starting materials and reagents for the synthesis of other products in chemical industry.

(ii) Formalin (40% solution of formaldehyde) solution is used to preserve biological specimens and in making bakelite, urea-formaldehyde glues and other polymeric products.

(iii) Acetaldehyde is used primarily as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.

(iv) Benzaldehyde is used in perfumery and dye industries. Some other are also known for their odours and flavours like butyraldehyde, camphor, vanillin, acetophenone, salicylaldehyde, cinnamaldehyde, etc.

(v) Some of the aldehydes and ketones are used for preparing materials like adhesives, paints, resins, perfumes, plastics, fabrics, etc.

TOPIC PRACTICE 1

OBJECTIVE Type Questions

1. Addition of water to butyne occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. The product formed is **NCERT Exemplar**

(a) $CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$

(b) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(c) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH+CO_2$

(d) $CH_3-\overset{O}{\overset{\|}{C}}-OH+H-\overset{O}{\overset{\|}{C}}-H$

2. In the reaction,

$$H_3C-CH=CH-CH_2-CH_2-CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH(i\text{-}Bu)_2}$$

Identify the product formed in the given reaction.

(a) $H_3C-CH_2CH_2CH_2CH_2CN$

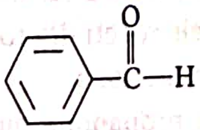
(b) $H_3C-CH=CH-CH_2CH_2CHO$

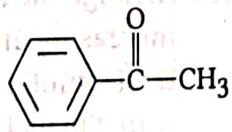
(c) $H_3CCH_2CH_2CH_2CH_2CHO$

(d) None of the above

3. Which of the following compounds is most reactive towards nucleophilic addition reactions? **NCERT Exemplar**

(a) $CH_3-\overset{O}{\overset{\|}{C}}-H$ (b) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(c) 

(d) 

4. Which of the following compounds will give butanone on oxidation with alkaline $KMnO_4$ solution? **NCERT Exemplar**

(a) Butan-1-ol

(b) Butan-2-ol

(c) Both (a) and (b)

(d) None of the above

5. The reagent which does not react with both, acetone and benzaldehyde? **NCERT Exemplar**

(a) Sodium hydrogen sulphite

(b) Phenyl hydrazine

(c) Fehling's solution

(d) Grignard reagent

6. Which of the following reagents is/are used in the given reaction? "$RCHO \longrightarrow RCOOH$"

(a) Nitric acid

(b) Potassium dichromate

(c) Tollen's reagent

(d) All of the above

7. In Clemmensen reduction, carbonyl compound is treated with .... **NCERT Exemplar**

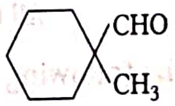
(a) zinc amalgam + HCl

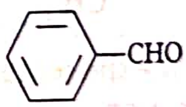
(b) sodium amalgam + HCl

(c) zinc amalgam + nitric acid

(d) sodium amalgam + HNO_3

8. Cannizzaro's reaction is not given by .... **NCERT Exemplar**

(a) 

(b) 

(c) HCHO

(d) CH_3CHO

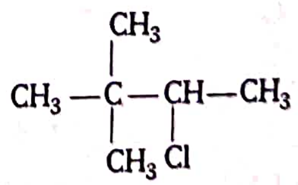
VERY SHORT ANSWER Type Questions

9. Write the IUPAC name of the following compound.

$$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{\overset{O}{\overset{\|}{C}}}-H$$

All India 2012

10. Write the IUPAC name of the following compound.



All India 2013

11. Draw the molecular structure of the compound 4-methylpent-3-en-2-one. **Delhi 2012; Foreign 2012**

12. Draw the structure of *p*-methylbenzaldehyde molecule. **Delhi 2013**

13. Draw the structure of 3-methylbutanal. **Delhi 2013**

14. How will you carry out the following conversion? Ethanol to acetone. **Delhi 2013**

15. Write the reagent required in the following reaction: **All India 2015**

$$CH_2{=}CH{-}CH_2OH \xrightarrow{?} CH_2{=}CH{-}CHO$$

16. Arrange the following compounds in the increasing order of their boiling points.

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$ **NCERT Intext; All India 2013**

17. Arrange the following compounds in the increasing order of their property as indicated: CH_3COCH_3, $C_6H_5COCH_3$, CH_3CHO (reactivity towards nucleophilic addition reaction) **All India 2015**

18. Write the mechanism of the following reaction.

$$CH_3CHO + HCN \xrightarrow{H^+} CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CN$$

19. Predict the product of the following reaction.

$$CH_3{-}\underset{\underset{CH_3}{|}}{C}{=}O \xrightarrow{NH_2-NH_2}$$

All India 2015

20. Name the reagent used in the following reaction.

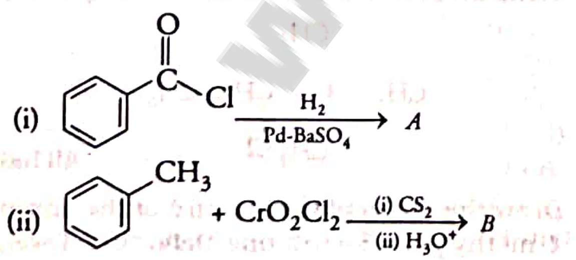
$$CH_3{-}CO{-}CH_3 \xrightarrow{?} CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CH_3$$

Delhi 2015

21. Give the simple chemical test to distinguish between ethanal and propanal. **Delhi 2013**

SHORT ANSWER Type I Questions

22. Consider the following reactions,



Write the product and name of the reaction.

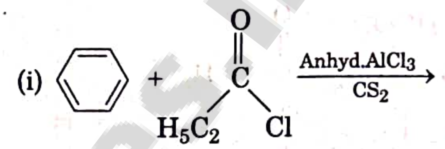
23. What is the use of chromyl chloride in the oxidation of methyl benzene?

24. Write the structure of major product(s) in the following: **All India 2019**

(i) $CH_3{-}CH_2{-}\underset{\underset{O}{||}}{C}{-}H \xrightarrow[\text{(ii) KOH, Glycol/heat}]{\text{(i) } H_2N-NH_2}$

(ii) $CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CHO \xrightarrow{\text{Conc. NaOH}}$

25. Draw the structures of products of the following reactions.



(ii) $(C_6H_5CH_2)_2Cd + 2CH_3COCl \longrightarrow$

(iii) $CH_3{-}C{\equiv}CH \xrightarrow{Hg^{2+}, H_2SO_4}$

26. Benzaldehyde can be obtained from benzal chloride. Write the reactions for obtaining benzal chloride and then benzaldehyde from it. **NCERT Exemplar**

27. Name the electrophile produced in the reaction of benzene with benzoyl chloride in the presence of anhydrous $AlCl_3$. Name the reaction also. **NCERT Exemplar**

28. Can Gattermann-Koch reaction be considered similar to Friedel-Crafts acylation? Discuss. **NCERT Exemplar**

29. Alkenes, $\rangle C{=}C\langle$ and carbonyl compounds, $\rangle C{=}O$ both contain a π-bond but alkenes show electrophilic addition reactions whereas carbonyl compounds show nucleophilic addition reactions. Explain. **NCERT Exemplar**

30. Arrange the following compounds in the increasing order of their reactivity towards nucleophilic addition reactions.

(i) Ethanal, propanal, propanone, butanone

(ii) Benzaldehyde, *p*-tolualdehyde, *p*-nitrobenzaldehyde, acetophenone

NCERT Intext

31. Complete the following reaction sequence.

$$CH_3{-}\overset{\overset{O}{||}}{C}{-}CH_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr} A \xrightarrow[\text{Ether}]{\text{Na metal}} B \xrightarrow{CH_3-Br} C$$

NCERT Exemplar

32. Predict the products of the following reactions.

(i) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O \xrightarrow[\text{KOH / Glycol, }\Delta]{H_2N-NH_2} ?$

(ii) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} ? + ?$ **Delhi 2015**

33. When liquid '*A*' is treated with a freshly prepared ammoniacal silver nitrate solution, it gives bright silver mirror. The liquid forms a white crystalline solid on treatment with sodium hydrogen sulphite. Liquid '*B*' also forms a white crystalline solid with sodium hydrogen sulphite but it does not give test with ammoniacal silver nitrate. Which of the two liquids is aldehyde? Write the chemical equations of these reactions also. **NCERT Exemplar**

34. Write the equations involved in the following reactions :
   (i) Wolff-Kishner reduction.
   (ii) Etard reaction. **Delhi 2017**

35. Write the reactions involved in the following reactions:
   (i) Clemmensen reduction
   (ii) Cannizzaro reaction **Delhi 2017**

36. Write the structural formulae and names of the four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde served as electrophile and which as nucleophile? **NCERT**

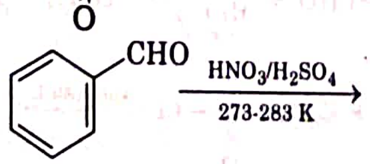
37. Give reasons to support the answer. **CBSE SQP (Term-II)**
   (i) Presence of alpha hydrogen in aldehydes and ketones is essential for aldol condensation.
   (ii) 3-hydroxypentan-2-one shows positive Tollen's test.

38. Ethyl benzene is generally prepared by acetylation of benzene followed by the reduction and not by direct alkylation. Think of a possible reason. **NCERT Exemplar**

39. Give the simple chemical tests to distinguish between
   (i) pentan-2-one and pentan-3-one
   (ii) ethanal and propanal **All India 2013**

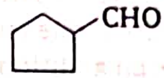
40. Complete the following reactions:

(i) $2H-\underset{\displaystyle O}{\underset{\|}{C}}-H \xrightarrow{\text{Conc. KOH}}$

(ii) 

Delhi 2013

SHORT ANSWER Type II Questions

41. Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give their common names.
   (i) $CH_3CO(CH_2)_4CH_3$
   (ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$
   (iii) $CH_3(CH_2)_5CHO$
   (iv) $Ph-CH=CH-CHO$
   (v) 

   (vi) PhCOPh **NCERT**

42. Draw the structures of the following derivatives.
   (i) 2,4-dinitrophenylhydrazone of benzaldehyde
   (ii) Cyclopropanone oxime
   (iii) Acetaldehyde dimethylacetal
   (iv) Semicarbazone of cyclobutanone
   (v) Ethylene ketal of hexan-3-one
   (vi) Methyl hemiacetal of formaldehyde **NCERT**

43. An alkene '*A*' (molecular formula C_5H_{10}) on ozonolysis gives a mixture of two compounds '*B*' and '*C*'. Compound '*B*' gives positive Fehling's test and also forms iodoform on treatment with I_2 and NaOH. Compound '*C*' does not give Fehling's test but forms iodoform. Identify the compounds *A*, *B* and *C*. Write the reaction for ozonolysis and formation of iodoform from *B* and *C*. **CBSE SQP (Term II)**

44. Give the names of the reagents to bring about the following transformations:
   (i) Pentan-1-ol to pentanal
   (ii) Cyclohexanol to cyclohexanone

45. Which of the following compounds would undergo aldol condensation and/or Cannizzaro reaction or neither of these two reactions. Write the structures of the expected products of aldol condensation or Cannizzaro reaction.
   (i) Methanal (ii) 2-methyl pentanal
   (iii) Benzaldehyde (iv) Benzophenone
   (v) Cyclohexanone (vi) 1-phenyl propanone
   (vii) Phenyl acetaldehyde (viii) Butan-1-ol
   (ix) 2,2-dimethyl butanal **NCERT**

46. How will you convert ethanal into the following compounds?
   (i) Butane-1,3-diol (ii) But-2-enal
   (iii) But-2-enoic acid **NCERT**

47. An organic compound with molecular formula $C_9H_{10}O$, forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro reaction.

On vigorous oxidation, it gives 1,2-benzene dicarboxylic acid. Identify the compound.

All India 2012; NCERT

48. An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphite and gives positive iodoform test.

On vigorous oxidation, it gives ethanoic acid and propanoic acid. Write the possible structure of the compound.

NCERT; All India 2009; Delhi 2008

49. A, *B* and *C* are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers *A* and *C* give positive Tollens' test whereas isomer *B* does not give Tollens' test, but gives positive iodoform test.

Isomers *A* and *B* on reduction with Zn(Hg)/conc. HCl give the same product *D*.

(i) Write the structures of *A*, *B*, *C* and *D*.

(ii) Out of *A*, *B* and *C* isomers, which one is least reactive towards addition of HCN?

CBSE 2018

LONG ANSWER Type Questions

50. (i) Write the products formed when CH_3CHO reacts with the following reagents:

(a) HCN

(b) $H_2N—OH$

(c) CH_3CHO in the presence of dilute NaOH.

(ii) Write the chemical equations to illustrate the following name reactions.

(a) Rosenmund's reduction

(b) Cannizzaro reaction

(iii) Out of $CH_3CH_2—CO—CH_2—CH_3$ and $CH_3CH_2—CH_2—CO—CH_3$, which gives iodoform test?

Delhi 2014

51. What will be formed, when the following reactions occur?

(i) Oxidation of alcohol

(ii) Oxidation of methyl benzene

(iii) Reduction of benzoyl chloride

(iv) Reduction of cyanide by AlH $(i\text{-Bu})_2$ and H_2O

(v) Dehydrogenation of alcohols

52. Predict the products formed when cyclohexane carbaldehyde reacts with following reagents:

(i) PhMgBr and then H_3O^+

(ii) Tollen's reagent

(iii) Semicarbazide and weak acid

(iv) Excess ethanol and acid

(v) Zinc amalgam and dilute hydrochloric acid

NCERT

53. (i) How will you bring about the following conversion in not more than two steps?

(a) Propanone to propene

(b) Ethanol to 3-hydroxybutanal

(c) Benzene to *m*-nitroacetophenone

(d) Bromobenzene to 1-phenylethanol

(e) Benzaldehyde to benzophenone

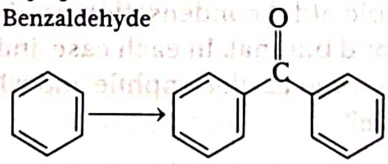
(f) Benzaldehyde to α-hydroxy phenylacetic acid

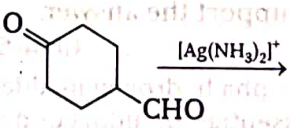
(ii) Arrange the following compounds in the increasing order of their property as indicated: Acetaldehyde, acetone, di-*tert*-butyl ketone, *tert*-butyl methyl ketone (reactivity towards HCN)

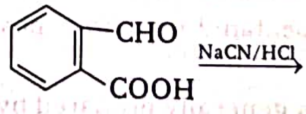
NCERT

54. Complete each synthesis by giving missing starting material, reagent or products.

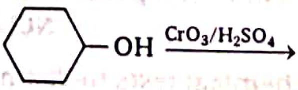
(i) $\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{H_2NCONHNH_2}$

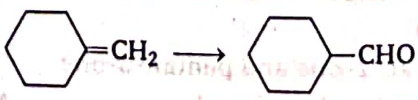
(ii) 

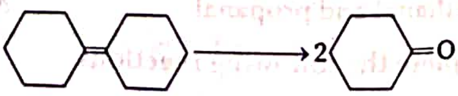
(iii) 

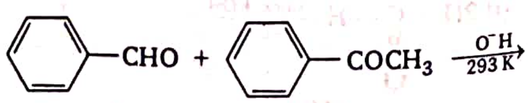
(iv) 

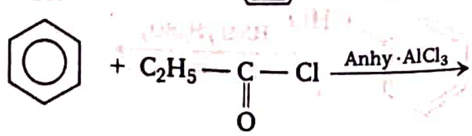
(v) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{\text{Dil. NaOH}}$

(vi) 

(vii) 

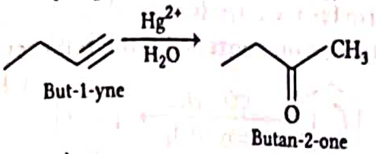
(viii) 

(ix) 

(x) 

HINTS AND EXPLANATIONS

1. (*b*) But-1-yne on reaction with water in presence of Hg^{2+} ions as a catalyst produces butan-2-one.



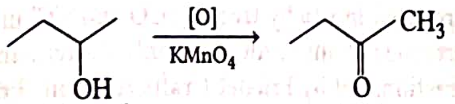
But-1-yne　　Butan-2-one

2. (*b*) In the reaction,

$$CH_3-CH=CH-CH_2-CH_2-CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) } AlH(i\text{-}Bu)_2} CH_3-CH=CH-CH_2-CH_2-CHO$$

3. (*a*) For carbonyl compounds greater the number of alkyl group lesser will be its electrophilicity. Hence, CH_3—CHO is most reactive towards nucleophilic addition reaction.

4. (*b*) Butan-2-ol on oxidation with alkaline $KMnO_4$ solution produces butanone as follows



Butan-2-ol　　Butan-2-one

5. (*c*) Acetone and benzaldehyde both do not react with Fehling's solution. Fehling's solution do not react with acetone as acetone is an ketone while benzaldehyde is an aromatic aldehyde having absence of α-hydrogen.

6. (*d*) Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate etc. Even mild oxidising agents, mainly Tollen's reagent and Fehling's reagent also oxidise aldehydes.

7. (*a*) Clemmensen reduction is used to convert carbonyl group to $>CH_2$ group as follows

$$>C=O \xrightarrow{Zn(Hg)+HCl} >CH_2$$

Zinc amalgam and HCl act as reagent in this reaction.

8. (*d*) Necessary condition for Cannizzaro reaction is absence of α-hydrogen atom. So, CH_3CHO will not give Cannizzaro reaction while other three compounds have no α-hydrogen. Hence, they will give Cannizzaro reaction.

9. Pent-2-en-1-al

10. 2-chloro-3,3-dimethylbutane

11. $\overset{1}{H_3C}-\overset{2}{C}(=O)-\overset{3}{CH}=\overset{4}{C}(CH_3)-\overset{5}{CH_3}$

4-methylpent-3-en-2-one

12. CHO

CH_3

p-methylbenzaldehyde

13. $\overset{4}{CH_3}-\overset{3}{CH}(CH_3)-\overset{2}{CH_2}-\overset{1}{CHO}$

3-methyl butanal

14. Ethanol to acetone

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{PCl_5} CH_3CH_2Cl \xrightarrow{KCN} CH_3CH_2CN$$

$$\xrightarrow{\text{Reduction}} CH_3CH_2CH_2NH_2 \xrightarrow[H_2O]{HNO_2}$$

$$CH_3CH_2CH_2OH \xrightarrow{PCl_5} CH_3CH_2CH_2Cl \xrightarrow[KOH]{Alc.}$$

$$CH_3CH=CH_2 \xrightarrow[Hg^{2+}]{Dil.\ H_2SO_4} \underset{\text{Acetone}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3}$$

15. Chromium base reagent like CrO_3 can be used for mild oxidation.

16. $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

Stronger the attractive forces, higher is the boiling point. Hydrocarbons are non-polar having weakest attractive forces, ethers are polar and aldehydes have strong dipolar interaction. Alcohols have maximum intermolecular forces due to the presence of H-bonding.

17. $C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$

$C_6H_5COCH_3$	CH_3COCH_3	CH_3CHO
+*I*-effect of phenyl and methyl groups increases electron density on CO group and steric hindrance caused by these two groups make nucleophilic attack difficult.	+*I*-effect of two alkyl groups and steric hindrance due to two bulky groups.	+*I*-effect of only one alkyl group and no sterically hindered group, making it more reactive towards nucleophilic attack.

18. $HCN + OH^- \rightleftharpoons :CN^- + H_2O$

$$H_3C-\overset{\displaystyle O}{\overset{\|}{C}}-H \overset{CN^-}{\rightleftharpoons} \underset{\text{Intermediate}}{CH_3-\overset{\displaystyle O^-}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-CN} \overset{H^+}{\rightleftharpoons} \underset{\text{Acetaldehyde cyanohydrin}}{CH_3-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-CN}$$

19. $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O \xrightarrow{H_2N-NH_2} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=NNH_2 + H_2O$

20. $\underset{\text{Propanone}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} \xrightarrow{NaBH_4} \underset{\text{Propan-2-ol}}{CH_3-\overset{\displaystyle OH}{\overset{|}{CH}}-CH_3}$

21. **Iodoform test** Ethanal, because of the presence of CH_3CO— skeleton gives iodoform test whereas propanal due to the absence of such a skeleton does not.

$$\underset{\substack{\text{Ethanal}\\ \text{or}\\ \text{Acetaldehyde}}}{CH_3CHO} + 4NaOH + 3I_2 \longrightarrow \underset{\substack{\text{Iodoform}\\ \text{(Yellow ppt)}}}{CHI_3\downarrow} + \underset{\text{Sodium formate}}{HCO\overset{-}{O}\overset{+}{Na}} + \underset{\substack{\text{Sodium}\\ \text{iodide}}}{3NaI} + 3H_2O$$

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + 4NaOH + 3I_2 \longrightarrow \text{No reaction}$$

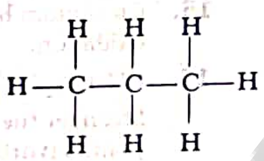
22. (i) Refer to text on page 312.
(ii) Refer to text on page 312.

23. Using CrO_2Cl_2 toluene gets oxidised to benzaldehyde.

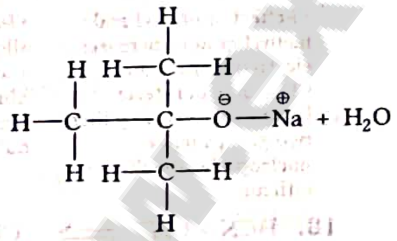
24. Structure of major product

(i) $CH_3—CH_2—\underset{\underset{O}{\|}}{C}—H \xrightarrow[\text{(ii) KOH, glycol / heat}]{\text{(i) } H_2N-NH_2}$

$\underset{\text{Propane}}{CH_3—CH_2—CH_3}$ Or



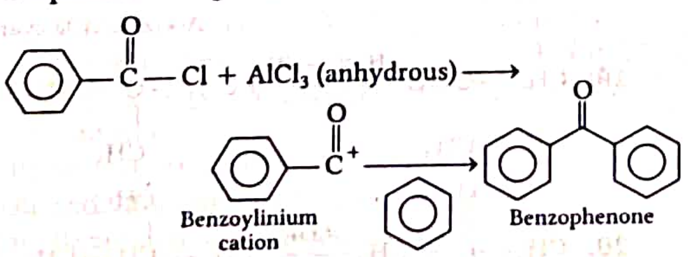
(ii) $CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CHO \xrightarrow{\text{Conc. NaOH}} (CH_3)_3COONa + H_2O$



25. (i) Refer to text on page 313.
(ii) Refer to text on page 313.
(iii) Refer to text on page 311.

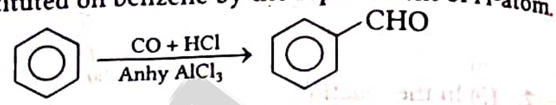
26. It is the commercial method for preparing benzaldehyde. Benzal chloride can be obtained by photochlorination of toluene, i.e. chlorination of toluene in the presence of sunlight. Then, benzal chloride on heating with boiling water, produces benzaldehyde as shown on page 313.

27. Benzene, on reaction with benzoyl chloride gives benzophenone through an intermediate benzoylinium cation.

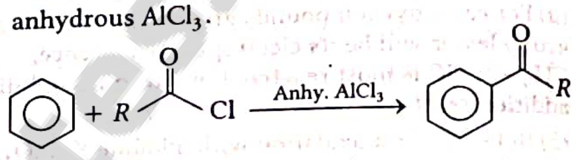


This is an example of **Friedel-Craft's acylation reaction.**

28. In Gattermann-Koch reaction, benzene or its derivative is treated with CO and HCl in the presence of anhydrous aluminium chloride to produce benzaldehyde. In this reaction, CO and HCl combine to form HCOCl, i.e. formyl chloride which gets substituted on benzene by the replacement of H-atom.



While in Friedel-Crafts acylation, acyl group is also transferred to carbon of benzene and acyl benzene is obtained as a result. This can be done by reaction of benzene with acyl chloride in the presence of anhydrous $AlCl_3$.



As, formyl chloride is unstable in nature. So, it can be prepared *in situ* by treating CO and HCl in the presence of anhy. $AlCl_3$ by only Gattermann-Koch reaction, not by Friedel-Crafts reaction. Since, in both the reactions, acylation takes place, hence, Gattermann-Koch reaction can be considered similar to Friedel-Crafts acylation.

29. Refer to text on page 314.

30. (i) Butanone < propanone < propanal < ethanal
(ii) Acetophenone < *p*-tolualdehyde < benzaldehyde < *p*-nitrobenzaldehyde

31.

$$CH_3—\overset{\overset{O}{\|}}{C}—CH_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgBr} \underset{(A)}{CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}—CH_3} \xrightarrow[\text{Ether}]{\text{Na metal}}$$

$$\underset{(B)}{CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{\overset{-}{O}\overset{+}{Na}}{|}}{C}}—CH_3} \xrightarrow[-NaBr]{CH_3-Br} \underset{\substack{(C)\\ \text{2-methyl-2-methoxy}\\ \text{propane}}}{CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{O—CH_3}{|}}{C}}—CH_3}$$

32. (i) $CH_3—\overset{\overset{O}{\|}}{C}—CH_3 \xrightarrow{NH_2—NH_2} \begin{matrix}H_3C\\ H_3C\end{matrix}\!\!>C=N—NH_2$

$\xrightarrow{\text{KOH/Ethylene glycol, }\Delta} \underset{\text{Propane}}{\begin{matrix}H_3C\\ H_3C\end{matrix}\!\!>CH_2}$

This is an example of Wolff-Kishner reduction.

(ii) $C_6H_5—CO—CH_3 \xrightarrow{NaOH/I_2} C_6H_5CO\overset{-}{O}\overset{+}{Na} + \underset{\text{Iodoform}}{CHI_3\downarrow}$

This is an example of haloform reaction.

33. Since, the liquid A reduces ammoniacal silver nitrate (Tollen's reagent), hence A is aldehyde and B does not give test with ammoniacal silver nitrate, thus, B is a ketone. Further, B forms a white crystalline solid on treatment with sodium hydrogen sulphite. This suggests that B is a methyl ketone.

- $$\underset{\text{Aldehyde or ketone}}{>C=O} + \underset{\text{Sodium hydrogen sulphite}}{NaHSO_3} \rightleftharpoons >C<^{OSO_2H}_{\overset{-}{O}\overset{+}{Na}} \xrightleftharpoons{\text{Proton transfer}} \underset{\text{Bisulphite addition compound (White crystalline solid)}}{>C<^{OSO_2Na}_{OH}}$$

- $$RCHO + 2[Ag(NH_3)_2]NO_3 + 2NH_4OH \longrightarrow RCOOH + \underset{\text{Silver mirror}}{2Ag\downarrow} + H_2O + 4NH_3 + 2NH_4NO_3$$

Note Aldehyde and ketone both gives white crystalline solid with sodium hydrogen sulphite but only aldehyde gives Tollen's test and Fehling's test.

34. (i) **Wolff-Kishner Reduction**
Refer to text on page 319.

(ii) **Etard Reaction**
Refer to text on page 312.

35. (i) **Clemmensen reduction**
Refer to text on page 319.

(ii) **Cannizzaro reaction**
Refer to text on page 321.

36. Four possible aldol condensation products are

(i) Propanal acts as both nucleophile and electrophile.

$$CH_3CH_2CHO + CH_3CH_2CHO \longrightarrow \underset{\text{3-hydroxy-2-methylpentanal}}{\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H(OH)-\overset{2}{C}H(CH_3)-\overset{1}{C}HO}$$

(ii) Butanal serves as both nucleophile and electrophile.

$$CH_3CH_2CH_2CHO + CH_3CH_2CH_2CHO \longrightarrow \underset{\text{2-ethyl-3-hydroxyhexanal}}{\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2-\overset{3}{C}H(OH)-\overset{2}{C}H(CH_2CH_3)\overset{1}{C}HO}$$

(iii) Propanal serves as electrophile and butanal as nucleophile.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{Butanal}}{CH_3CH_2CH_2CHO} \longrightarrow \underset{\text{2-ethyl-3-hydroxypentanal}}{\overset{5}{C}H_3\overset{4}{C}H_2-\overset{3}{C}H(OH)-\overset{2}{C}H(CH_2CH_3)\overset{1}{C}HO}$$

(iv) Butanal serves as electrophile and propanal as nucleophile.

$$\underset{\text{Butanal}}{CH_3CH_2CH_2CHO} + \underset{\text{Propanal}}{CH_3CH_2CHO} \longrightarrow \underset{\text{3-hydroxy-2-methyl-hexanal}}{\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2-\overset{3}{C}H(OH)-\overset{2}{C}H(CH_3)-\overset{1}{C}HO}$$

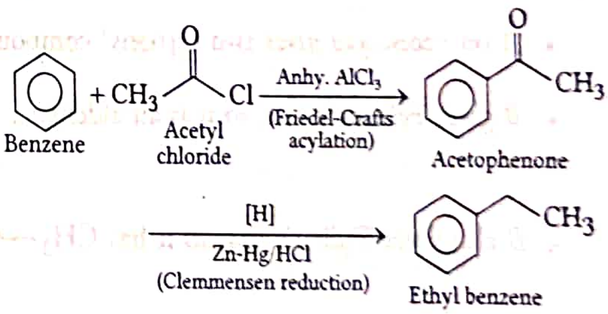
37. (i) The presence of alpha hydrogen in aldehydes and ketones is essential for aldol condensation because they are acidic in nature (due to the presence of electron withdrawing carbonyl group). As a result, the electron density at alpha C—H bond decreases and hence, H-atom becomes weakly held which can be easily abstracted by strong bases forming enolate ion, which are stabilised by resonance.

(ii) The structure of 3-hydroxypentan-2-one is

$$\overset{5}{C}H_3\overset{4}{C}H_2-\overset{3}{C}H(OH)-\overset{2}{C}(=O)-\overset{1}{C}H_3$$

All alpha hydroxy ketones gives Tollen's test. Since, α-hydroxy ketones have the ability to tautomerises to aldehydes and aldehydes gives Tollen's test. The given compound is also a α-hydroxy ketone. Thus, it gives this test.

38. Preparation of ethyl benzene from acylation of benzene yields acetophenone which on reduction gives ethyl benzene. The complete reactions can be shown as:



The direct alkylation cannot be performed because polysubstitution product is formed.

Due to disadvantage of polysubstitution, the Friedel-Crafts alkylation reaction is not used for the preparation of alkyl benzene. Instead of that, Friedel-Crafts acylation is used.

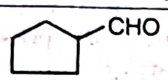
39. (i) **Distinguishing test between pentan-2-one and pentan-3-one** Pentan-2-one responds positively towards iodoform test whereas pentan-3-one ($C_2H_5COC_2H_5$), due to the absence of $-\overset{O}{\overset{\|}{C}}-CH_3$ group, do not give iodoform test.

$$\underset{\text{Pentan-2-one}}{\overset{1}{C}H_3-\overset{2}{C}O-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_3} + 3NaOH \xrightarrow[\text{Heat}]{I_2} \underset{\text{Yellow ppt.}}{CHI_3} + CH_3CH_2CH_2CO\bar{O}\overset{+}{Na} + 2NaOH$$

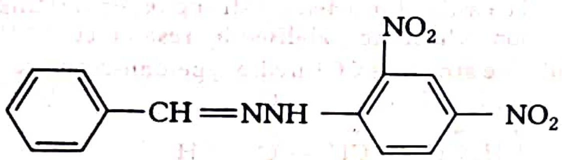
(ii) **Distinguishing test between ethanal and propanal** (Iodoform test) Refer to solution 21 on page 327.

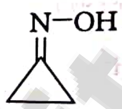
40. (i) Refer to text on page 321. (ii) Refer to text on page 322.

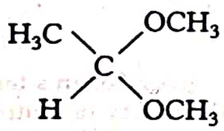
41.

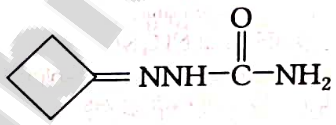
S.No.	Structure	IUPAC name	Common name
(i)	$CH_3CO(CH_2)_4CH_3$	Heptan- 2-one	Methyl *n*-pentyl ketone
(ii)	$CH_3CH_2CHBrCH_2CH(CH_3)CHO$	4-bromo-2-methylhexanal	γ-bromo- α-methyl caproaldehyde
(iii)	$CH_3(CH_2)_5CHO$	Heptanal	Heptanaldehyde
(iv)	Ph— CH ═ CH— CHO	3-phenylprop -2-enal	β-phenylacrolein
(v)		Cyclopentane carbaldehyde	Cyclopentane carbaldehyde
(vi)	PhCOPh	Diphenylmethanone	Benzophenone

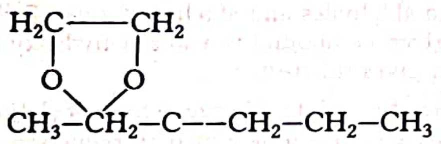
42.

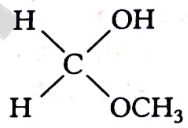
(i) 

(ii) 

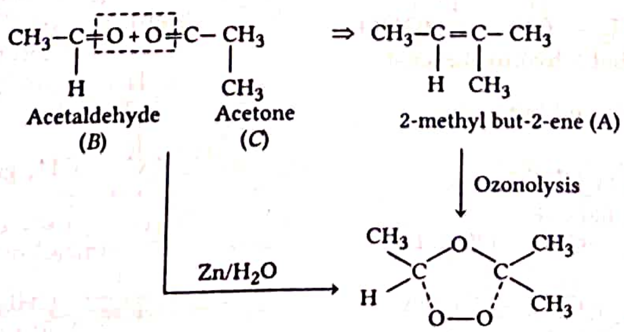
(iii) 

(iv) 

(v) 

(vi) 

43.
- According to the given information compound *A* (mol. formula C_5H_{10}) is an alkene.
- *A* on ozonolysis gives two carbonyl compound. (i.e. have $>C=O$ group) *B* and *C*.
- *B* gives Fehling's test, so it is an aldehyde.
- *B* also gives Tollen's test, so it has $CH_3-\overset{O}{\overset{\|}{C}}-$ group. That means, *B* is acetaldehyde.
- *C* does not give Fehling test, so it is a ketone. Also, it gives positive iodoform test so it contain $CH_3-\overset{O}{\overset{\|}{C}}-$ group.
- Now, structure of alkene *A* can be obtained by writing the products of ozonolysis side by side with their $>C=O$ groups facing each other. On removing the oxygen atoms and joining the remaining fragments by a double bond, the structure of alkene '*A*' can be obtained which is 2-methylbut-2-ene.



- **Fehling's test**

$$\underset{(B)}{CH_3CHO} + 2Cu^{2+} + 5\overset{-}{O}H \longrightarrow CH_3COO^- + \underset{\text{(Red ppt.)}}{Cu_2O} + 3H_2O$$

$$CH_3COCH_3 + 2Cu^{2+} + 5\overset{-}{O}H \longrightarrow \text{No reaction}$$

- **Iodoform reaction**

$$\underset{(B)}{CH_3CHO} + 3I_2 + NaOH \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3\downarrow} + 3HI + HCO\overset{-}{O}\overset{+}{Na}$$

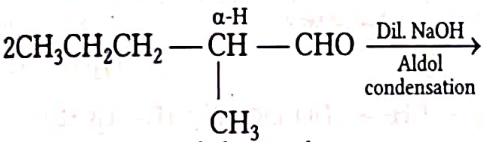
$$\underset{(C)}{CH_3-\overset{\overset{\large O}{\|}}{C}-CH_3} + 3I_2 + 4NaOH \longrightarrow \underset{\text{(Yellow ppt.)}}{CHI_3\downarrow} + CH_3CO\overset{-}{O}\overset{+}{Na} + 3NaI + 3H_2O$$

$\therefore A = CH_3CH{=}C(CH_3)_2$: 2-methylbut-2-ene
$B = CH_3CHO$: Acetaldehyde
$C = CH_3COCH_3$: Acetone

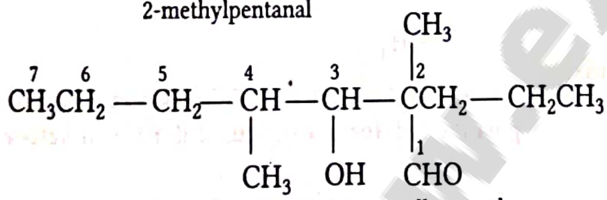
44. (i) Refer to text on page 310.
(ii) Refer to text on page 310.

45. Compounds which undergo aldol condensation (having α-hydrogen atom) are follows :

(ii) **2-methyl pentanal**

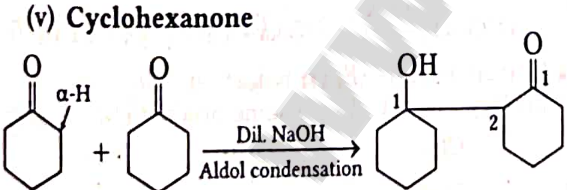


2-methylpentanal



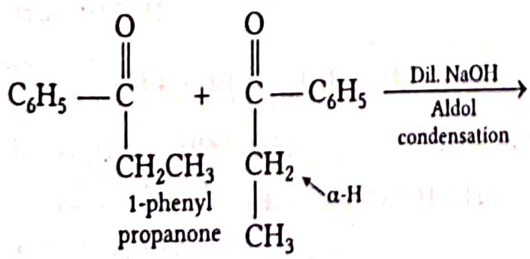
3-hydroxy-2, 4-dimethyl 2-propylheptanal

(v) **Cyclohexanone**

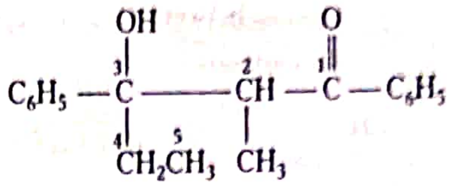


Cyclohexanone 2-(1-hydroxy-1-cyclohexyl) cyclohexan-1-one

(vi) **1-phenyl propanone**

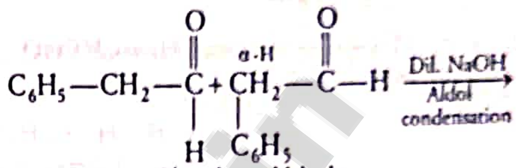


1-phenyl propanone

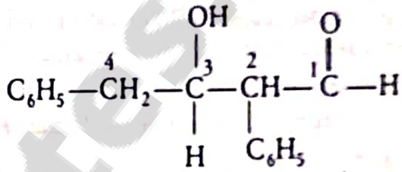


3-hydroxy-2-methyl-1, 3-diphenylpentan-1-one

(vii) **Phenyl acetaldehyde**



Phenyl acetaldehyde



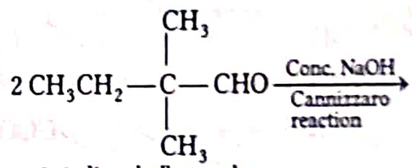
3-hydroxy-2,4-diphenylbutanal

Compounds which undergo Cannizzaro reaction (only aldehydes without α-hydrogen atoms)

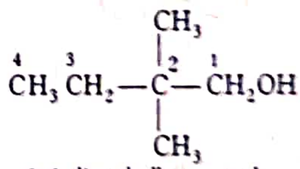
(i) **Methanal** Refer to text page 321.

(iii) **Benzaldehyde** Refer to text on page 321.

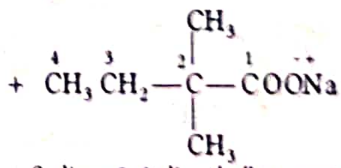
(ix) **2,2-dimethyl butanal**



2, 2-dimethylbutanal



2, 2-dimethylbutan-1-ol



Sodium-2, 2-dimethylbutanoate

Compounds which undergo neither Cannizzaro nor Aldol reaction.

(iv) **Benzophenone** It is a ketone, so it does not undergo Cannizzaro reaction without α-hydrogen. It cannot participate in Aldol condensation.

(viii) **Butan-1-ol** It is an alcohol. So, it cannot participate in any of the above two reactions.

46. (i) $2CH_3CHO \xrightarrow[\text{(Aldol condensation)}]{\text{Dil. NaOH}}$ (Ethanal)

$\overset{4}{C}H_3\overset{3}{C}HOH—\overset{2}{C}H_2—\overset{1}{C}HO \xrightarrow[\text{(Reduction)}]{NaBH_4}$ (3-hydroxybutanal)

$\overset{4}{C}H_3—\overset{3}{C}HOH—\overset{2}{C}H_2—\overset{1}{C}H_2OH$ (Butane-1, 3-diol)

(ii) Refer to text on page 320.

(iii) $2CH_3CHO \xrightarrow[\text{(ii)} -H_2O,\ \Delta]{\text{(i) Dil. NaOH}} CH_3CH=CHCHO$ (Ethanal)

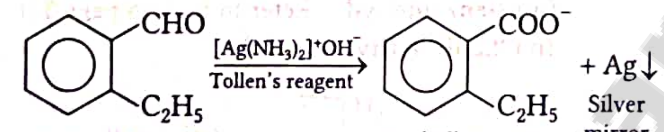
$\xrightarrow{\text{Alk. }KMnO_4} CH_3CH=CHCO_2H$ (But-2-enoic acid)

47. (i) As the given compound with molecular formula $C_9H_{10}O$, forms a 2,4-DNP derivative and reduces Tollen's reagent, thus it must be an aldehyde.

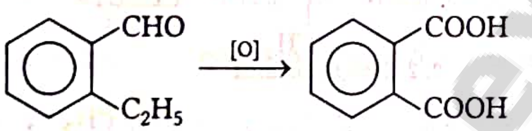
(ii) As it undergoes Cannizzaro reaction, hence — CHO group is directly attached to the benzene ring.

(iii) On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Therefore, it must be an *ortho*-substituted benzaldehyde and the only *o*-substituted aromatic aldehyde which have $C_9H_{10}O$ molecular formula is *o*-ethyl benzaldehyde.

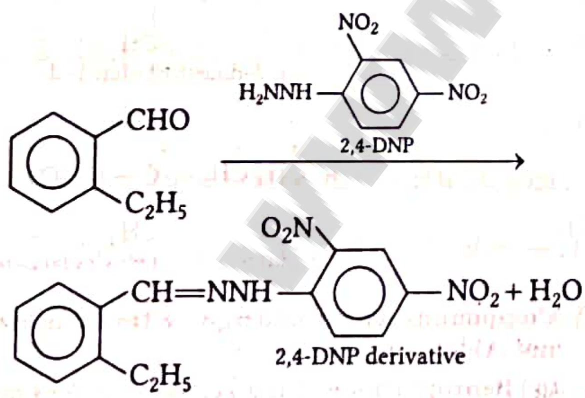
Reactions involved



o-ethyl benzaldehyde   2-ethylbenzoate



1, 2-benzene dicarboxylic acid



2,4-DNP derivative

48. C = 69.77%, H = 11.63%, O = 100 – (69.77 + 11.63) = 18.6%

Element	Percentage (x)	Molar mass (y)	Moles (x/y)	Simple ratio
C	69.77	12	5.81	5
H	11.63	1	11.63	10
O	18.60	16	1.16	1

Empirical formula of given compound = $C_5H_{10}O$

Empirical formula mass = $5\times 12 + 10\times 1 + 1\times 16 = 86$

$$n = \frac{86}{86} = 1$$

$\therefore$ Molecular formula = $(C_5H_{10}O)_1 = C_5H_{10}O$

Since, it does not give Tollen's test but gives positive iodoform test, hence it is a methyl ketone, i.e. have — $COCH_3$ group. Since, on oxidation, it gives ethanoic acid and propanoic acid, it is pentan-2-one.

$$\underset{\text{Pentan-2-one}}{CH_3—\underset{\underset{O}{\|}}{C}—CH_2CH_2CH_3} \xrightarrow{[O]} CH_3COOH + CH_3CH_2COOH$$

Hence, the compound is pentan-2-one.

49. (i) The possible functional isomers of carbonyl compound with molecular formula, C_4H_8O are

$$CH_3—\overset{\overset{CH_3}{|}}{C}H—CHO,\ CH_3CH_2CH_2CHO,$$

$$CH_3CH_2—\overset{\overset{O}{\|}}{C}—CH_3$$

- Isomers (*A*) and (*C*) gives positive Tollen's test, thus they must be aldehydes.

$$\underset{\text{Aldehyde}}{RCHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+} \xrightarrow{\Delta} RCOO^- + \underset{\text{Silver mirror}}{2Ag\downarrow} + 2H_2O + 4NH_3\uparrow$$

$$CH_3—\underset{\underset{CH_3}{|}}{C}H—CHO \text{ and } CH_3CH_2CH_2CHO$$

- Isomer (*B*) does not give Tollen's test, but gives positive Iodoform test, thus it must be a ketone with $CH_3\overset{\overset{O}{\|}}{C}—$ group.

$$RCOCH_3 \xrightarrow{NaOX} RCOONa + CHX_3 \quad [X = Cl, Br, I]$$

- Isomers (*A*) and (*B*) on reduction with Zn(Hg)/ conc. HCl give same product (*D*)

$$CH_3—\overset{\overset{CH_3}{|}}{C}H—CHO + 4[H] \xrightarrow{\text{Zn-Hg/conc. HCl}} CH_3\overset{\overset{CH_3}{|}}{C}H—CH_3 + H_2O$$

$$CH_3—CH_2—CH_2—CHO + 4[H] \xrightarrow{\text{Zn-Hg/conc. HCl}} CH_3—CH_2—CH_2—CH_3 + H_2O$$

$$CH_3CH_2COCH_3 + 4[H] \xrightarrow{\text{Zn-Hg/conc. HCl}} CH_3CH_2CH_2CH_3 + H_2O$$

So the structures of (*A*), (*B*), (*C*) and (*D*) are :

$\underset{(A)}{CH_3CH_2CH_2CHO}$, $\underset{(B)}{CH_3CH_2COCH_3}$,

$$\underset{(C)}{CH_3\underset{\displaystyle}{\overset{\displaystyle CH_3}{\overset{|}{C}}}H-CHO}\ ,\ \underset{(D)}{CH_3CH_2CH_2CH_3}$$

(ii) The isomer (*B*) is least reactive towards addition of HCN. Since, aldehydes are more reactive towards nucleophilic addition reactions than ketones due to inductive and steric effects.

50. (i) (a) Refer to text on page 315.
(b) Refer to text on page 317.
(c) Refer to text on page 320.

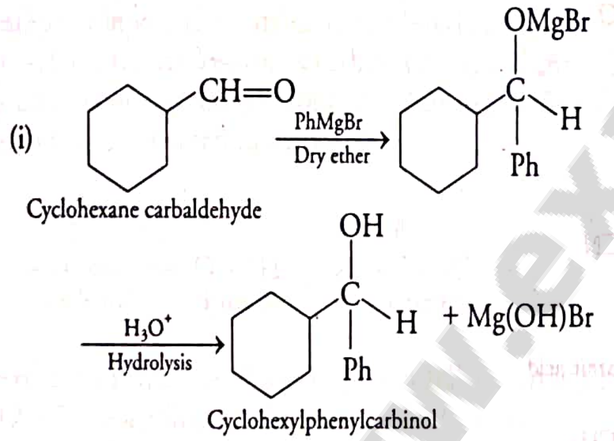
(ii) (a) **Rosenmund's reduction** Refer to text on page 312.
(b) **Cannizzaro reaction** Refer to text on page 321.

(iii) $CH_3CH_2-CH_2-CO-CH_3$ gives iodoform test as it contains CH_3CO- group.

51. (i) Refer to text on page 310.
(ii) Refer to text on page 312.
(iii) Refer to text on page 312.
(iv) Refer to text on page 312.
(v) Refer to text on page 310.

52.

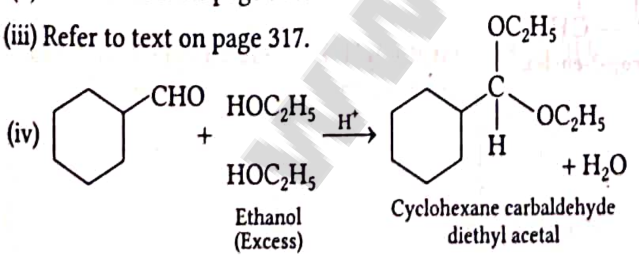
(i)



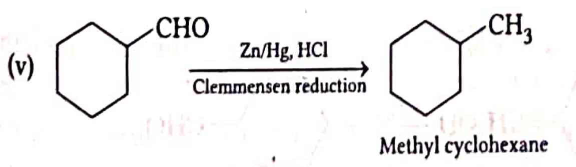
(ii) Refer to text on page 318.

(iii) Refer to text on page 317.

(iv)



(v)



53. (i) (a) **Propanone to propene**

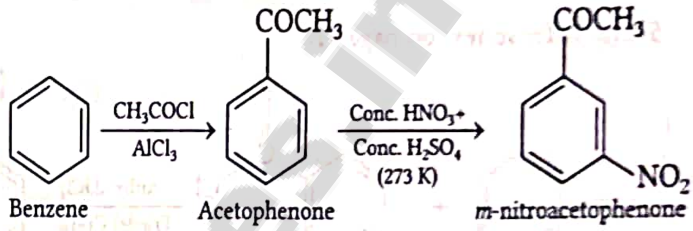
$$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow[2[H]]{LiAlH_4} \underset{\text{Propan-2-ol}}{CH_3\underset{OH}{\underset{|}{C}}HCH_3} \xrightarrow[\text{Heat}]{H_2SO_4\text{ (conc.)}} \underset{\text{Propene}}{CH_3CH{=}CH_2}$$

(b) **Ethanol to 3-hydroxybutanal**

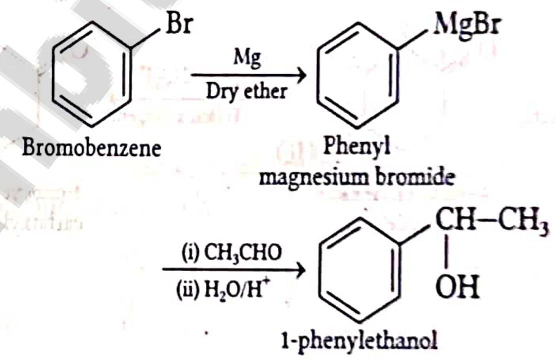
$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[CrO_3\text{ in anhy. medium}]{\text{Oxidation}} \underset{\text{Ethanal}}{CH_3CHO}$$

$$\xrightarrow[\text{condensation}]{\text{Aldol}} \underset{\substack{\text{3-hydroxybutanal} \\ \text{(formed from 2 molecules of ethanal)}}}{CH_3\underset{OH}{\underset{|}{C}}HCH_2CHO}$$

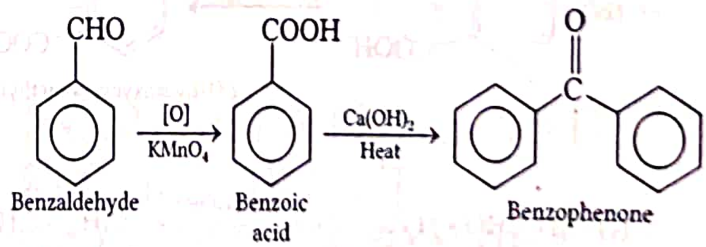
(c) **Benzene to *m*-nitroacetophenone**



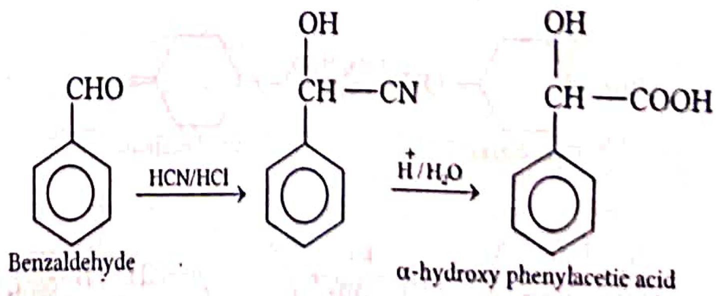
(d) **Bromobenzene to 1-phenylethanol**



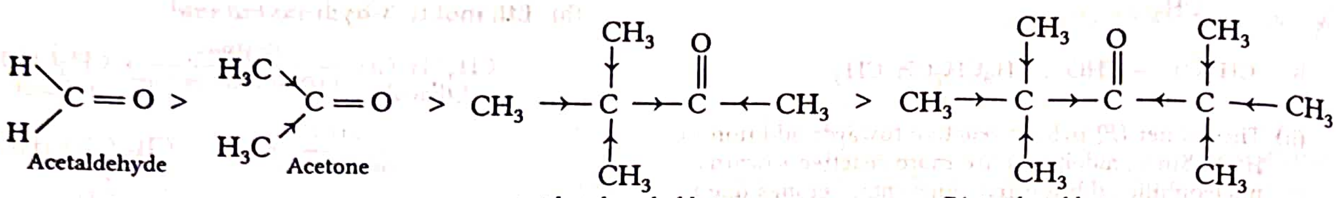
(e) **Benzaldehyde to benzophenone**



(f) **Benzaldehyde to α-hydroxyphenylacetic acid**



(ii) The reactivity of carbonyl compounds towards HCN addition decreases as the +*I*-effect of the alkyl group(s) increases or the presence of bulkier alkyl group increases, which causes steric hindrance to the nucleophilic attack by CN^- at the carbonyl carbon. Thus, the reactivity decreases in the order:

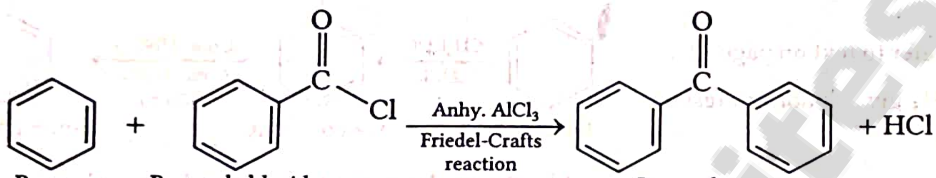


Acetaldehyde > Acetone > *tert*-butyl methyl ketone > Di-*tert*-butyl ketone

$+I$-effect increases →
Steric hindrance due to bulkier group increases →
Reactivity towards HCN addition reaction decreases →

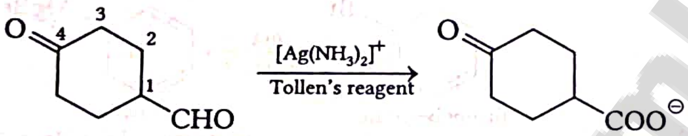
54. (i) Refer to text on page 317.

(ii)



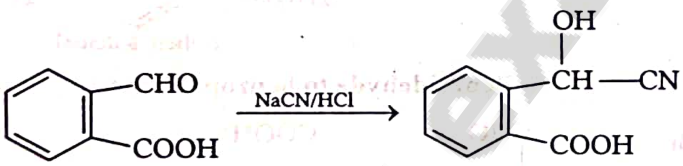
Benzene + Benzoyl chloride $\xrightarrow[\text{Friedel-Crafts reaction}]{\text{Anhy. } AlCl_3}$ Benzophenone + HCl

(iii)



4-oxocyclohexane carbaldehyde $\xrightarrow[\text{Tollen's reagent}]{[Ag(NH_3)_2]^+}$ 4-oxocyclohexane carboxylate anion

(iv)

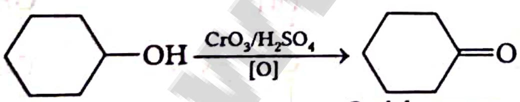


2-(1-hydroxycyanomethyl) benzoic acid

(v) $C_6H_5CHO + H_2\overset{\overset{\displaystyle CH_3}{|}}{C}-CHO \xrightarrow{\text{Dil. NaOH}/\Delta} C_6H_5-\overset{3}{C}H=\overset{\overset{\displaystyle CH_3}{|}}{\underset{2}{C}}-\overset{1}{C}HO$

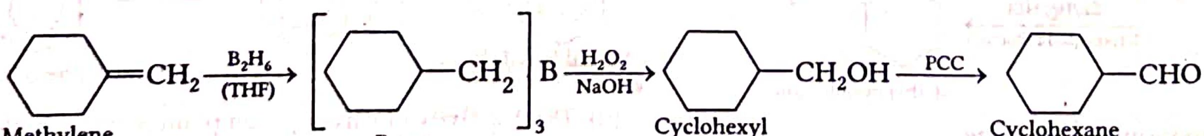
Propanal; 2-methyl-3-phenylprop-2-en-1-al

(vi)

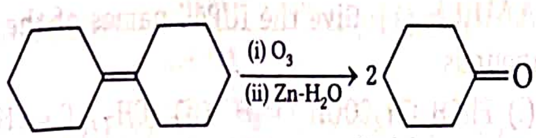


Cyclohexanol $\xrightarrow[\text{[O]}]{CrO_3/H_2SO_4}$ Cyclohexanone

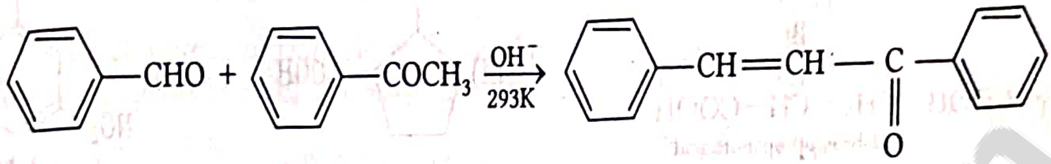
(vii)



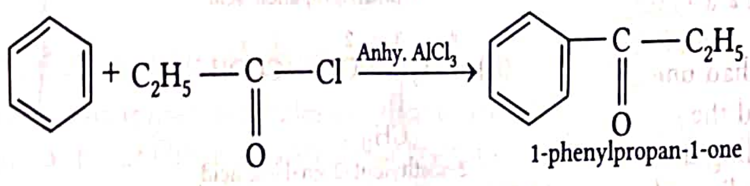
Methylene cyclohexane $\xrightarrow[\text{(THF)}]{B_2H_6}$ Borane $\xrightarrow[\text{NaOH}]{H_2O_2}$ Cyclohexyl methanol $\xrightarrow{\text{PCC}}$ Cyclohexane carbaldehyde

(viii) 

Cyclohexanone

(ix) 

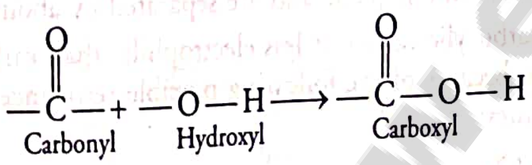
Benzal acetophenone

(x) 

1-phenylpropan-1-one

|TOPIC 2| Carboxylic Acids

The carbon compounds containing a carboxyl functional group, —COOH are known as carboxylic acids. Carboxyl group consists of a carbonyl group attached to a hydroxyl group, hence it is named as carboxyl.

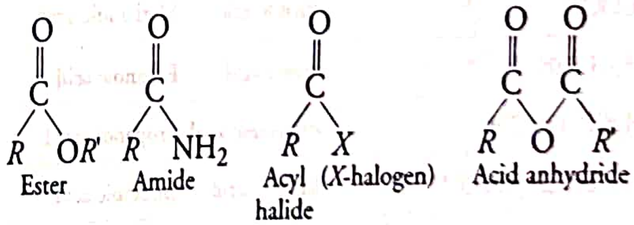


Carboxylic acids may be aliphatic (*R*COOH) or aromatic (ArCOOH) depending on the groups, alkyl or aryl, attached to carboxylic carbon.

e.g. $CH_3CH_2CH_2COOH$ Butanoic acid CH_3COOH Ethanoic acid

Benzoic acid

Some higher members of aliphatic carboxylic acids (C_{12} -C_{18}) known as fatty acids, occur in natural fats as esters of glycerol. When carbonyl group gets attached with groups like —O*R*, —NH_2, —*X* and —OCO*R*, the compounds are called derivatives of carboxylic acids and known by the name, ester, amide, acyl halide and acid anhydride respectively.



NOMENCLATURE AND STRUCTURE OF CARBOXYL GROUP

Nomenclature

Carboxylic acids are named by two systems:

Common system In common system, the common names end with the suffix -'ic acid' and have been derived from Latin or Greek names of their natural sources. e.g. Formic acid (HCOOH) was first obtained from red ants (Latin : *formica* means ant), acetic acid (CH_3COOH) from vinegar (Latin : *acetum* means vinegar), butyric acid ($CH_3CH_2CH_2COOH$) from rancid butter (Latin : *butyrum* means butter).

IUPAC system IUPAC name of carboxylic acid is alkanoic acid. Thus, in IUPAC system, their names are derived by replacing the terminal 'e' from the name of corresponding straight chain alkane by suffix 'oic acid'. In numbering, the carbon chain, the carboxylic carbon is numbered one.

e.g.

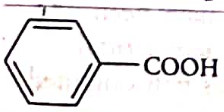
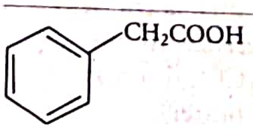
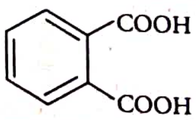
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-COOH$
3-methylbutanoic acid

$CH_3-\overset{\displaystyle Br}{\overset{|}{CH}}-COOH$
2-bromopropanoic acid

$C_6H_5-CH=CH-COOH$
3-phenylprop-2-enoic acid

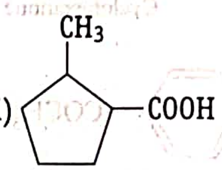
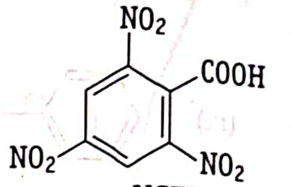
For naming the compounds containing more than one carboxyl group, the alkyl chain is numbered and the number of carboxyl groups are indicated by adding the multiplicative prefix dicarboxylic acid, tricarboxylic acid, etc., to the name of parent alkyl chain. The position of $-COOH$ groups are indicated by the arabic numeral before the multiplicative prefix.

IUPAC names and structures of some carboxylic acids

Structure	Common name	IUPAC name
$HCOOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
$(CH_3)_2CHCOOH$	*iso*-butyric acid	2-methylpropanoic acid
$HOOC-COOH$	Oxalic acid	Ethanedioic acid
$HOOC-CH_2-COOH$	Malonic acid	Propanedioic acid
$HOOC-(CH_2)_2-COOH$	Succinic acid	Butanedioic acid
$HOOC-(CH_2)_3-COOH$	Glutaric acid	Pentanedioic acid
$HOOC-(CH_2)_4-COOH$	Adipic acid	Hexanedioic acid
$HOOC-CH_2-CH(COOH)-CH_2-COOH$	—	Propane-1,2,3-tricarboxylic acid
	Benzoic acid	Benzene carboxylic acid (Benzoic acid)
	Phenylacetic acid	2-phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

EXAMPLE |1| Give the IUPAC names of the following compounds.

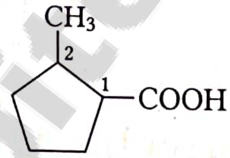
(i) $PhCH_2CH_2COOH$ (ii) $(CH_3)_2C=CHCOOH$

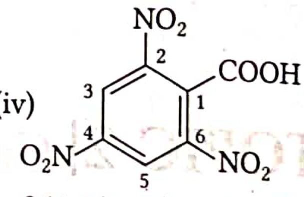
(iii)  (iv) 

NCERT Intext

Sol. (i) $\overset{3}{Ph-CH_2}-\overset{2}{CH_2}-\overset{1}{COOH}$
3-phenylpropanoic acid

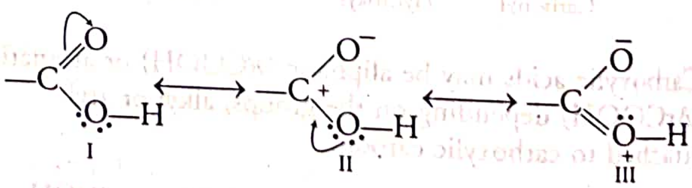
(ii) $\overset{4}{CH_3}\underset{\displaystyle CH_3}{\underset{|}{\overset{3}{C}}}=\overset{2}{CH}-\overset{1}{COOH}$
3-methylbut-2-en-1-oic acid

(iii) 
2-methylcyclopentane carboxylic acid

(iv) 
2,4,6-trinitrobenzoic acid

Structure

In carboxylic acids, the bonds attached to the carboxyl carbon are in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon because of the following possible resonance structures:



In structures (I) and (III), carboxyl carbon is electrically neutral. As a result, the carboxyl carbon of resonance hybrid is less positive. However, like carbonyl group, carboxyl group is also polar due to the resonance structures (II) and (III).

METHODS OF PREPARATION

Carboxylic acids are prepared by the following methods:

From Primary Alcohols and Aldehydes

Primary alcohols and aldehydes are readily oxidised to corresponding carboxylic acids with common oxidising agents such as potassium permanganate ($KMnO_4$) in neutral, acidic or alkaline medium or by potassium dichromate ($K_2Cr_2O_7$) and chromium trioxide (CrO_3) in acidic medium (Jones reagent).

$$RCH_2OH \xrightarrow[\text{(ii)}H_3O^+]{\text{(i) Alkaline } KMnO_4} RCOOH$$

$$\underset{\text{Decan-1-ol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow{CrO_3,\,H_2SO_4} \underset{\text{Decanoic acid}}{CH_3(CH_2)_8COOH}$$

Carboxylic acids are also prepared from aldehydes by the use of mild oxidising agents like Tollen's reagent.

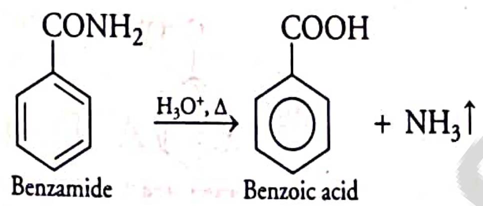
$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\text{Tollen's reagent}]{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

From Nitriles and Amides

Nitriles are first hydrolysed to amides and then to acids in the presence of $\overset{+}{H}$ or $\bar{O}H$ as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.

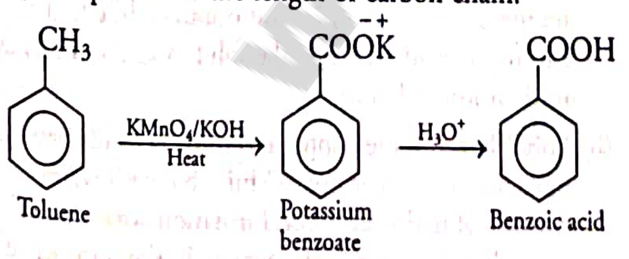
$$R{-}CN \xrightarrow[H_2O]{\overset{+}{H}\text{ or }\bar{O}H} R{-}\overset{\overset{\large O}{\|}}{C}{-}NH_2 \xrightarrow[\Delta]{\overset{+}{H}\text{ or }\bar{O}H} RCOOH + NH_3\uparrow$$

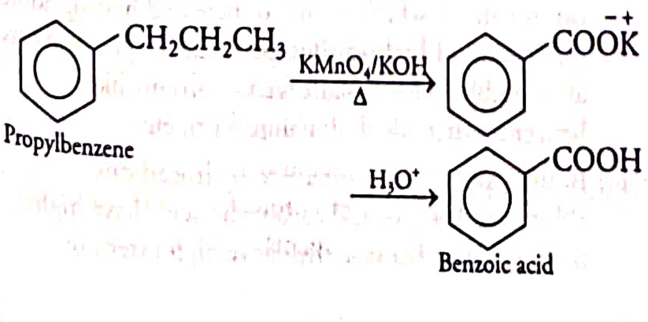
$$\underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[H_3O^+]{\Delta} \underset{\text{Ethanoic acid}}{CH_3COOH} + NH_3\uparrow$$



From Alkylbenzenes

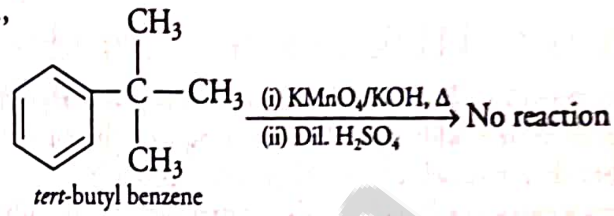
Aromatic acids are obtained by vigorous oxidation of alkyl benzene with chromic acids or acidic or alkaline $KMnO_4$. During oxidation, the aromatic nucleus remains intact but the entire chain is oxidised to —COOH group irrespective of the length of carbon chain.





1° and 2° alkyl chains contain benzylic hydrogen so, these are oxidised to carboxyl groups while 3° alkyl chains contain no benzylic hydrogen so, these are not oxidised.

e.g.,



Same oxidising agents can be used to oxidise alkenes to carboxylic acids.

e.g.

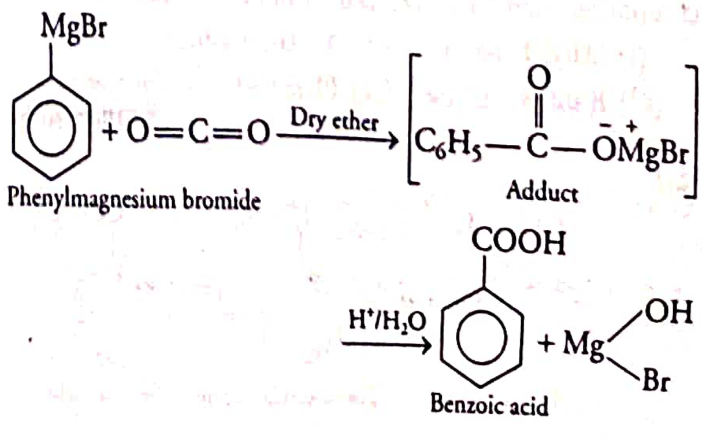
$$\underset{\text{But-2-ene}}{CH_3CH=CHCH_3} \xrightarrow[\text{Dil. } H_2SO_4]{KMnO_4/KOH,\,\Delta} \underset{\text{Ethanoic acid}}{2CH_3COOH}$$

From Grignard Reagents

Grignard reagents react with dry ice (CO_2) in ethereal solution to produce salts of carboxylic acids, which on acidification with mineral acids give corresponding carboxylic acids.

$$R{-}MgX + O{=}C{=}O \xrightarrow{\text{Dry ether}} \underset{\text{Adduct}}{R{-}\underset{\underset{\large O}{\|}}{C}{-}\bar{O}\overset{+}{M}gX} \xrightarrow[-Mg(OH)X]{H^+/H_2O} R{-}COOH$$

$$\underset{\text{Methyl magnesium bromide}}{CH_3MgBr} + O{=}C{=}O \xrightarrow{\text{Dry ether}} \underset{\text{Addition product}}{\left[CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}\bar{O}\overset{+}{M}gBr\right]} \xrightarrow{H^+/H_2O} \underset{\text{Ethanoic acid}}{CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}OH} + Mg\begin{smallmatrix}OH\\Br\end{smallmatrix}$$



Note As nitriles and Grignard reagents can be prepared from alkyl halides, thus, the last two methods (from alkyl benzenes and Grignard reagents) listed above are very useful for converting alkyl halides into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides (i.e. ascending the series).

From Acyl Halides and Anhydrides

Acid chlorides when hydrolysed with water give carboxylic acids or more readily hydrolysed with aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids. Anhydrides on the other hand are hydrolysed to corresponding acids with water.

$$RCOCl \xrightarrow{H_2O} RCOOH + Cl^-$$

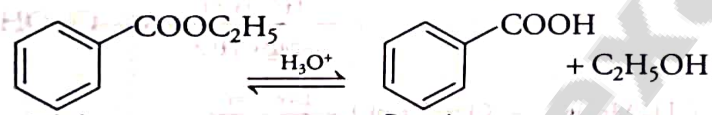
$$RCOCl \xrightarrow{\bar{O}H/H_2O} RCOO^- + \bar{Cl} \xrightarrow{H_3O^+} RCOOH$$

$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{2C_6H_5COOH}$$

$$\underset{\text{Benzoic ethanoic anhydride}}{C_6H_5COOCOCH_3} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Ethanoic acid}}{CH_3COOH}$$

From Esters

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids.



Ethyl benzoate   Benzoic acid

$$\underset{\text{Ethyl butanoate}}{CH_3CH_2CH_2COOC_2H_5} \underset{}{\xrightarrow{NaOH}} CH_3CH_2CH_2CO\bar{O}\overset{+}{Na} + C_2H_5OH$$

$$\xrightarrow{H_3O^+} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

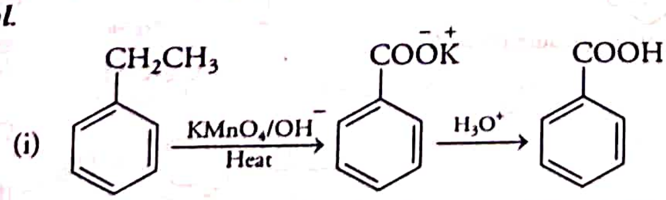
EXAMPLE |2| Show how each of the following compounds can be converted to benzoic acid?

(i) Ethyl benzene (ii) Acetophenone
(iii) Bromobenzene (iv) Phenylethene (styrene)

NCERT Intext

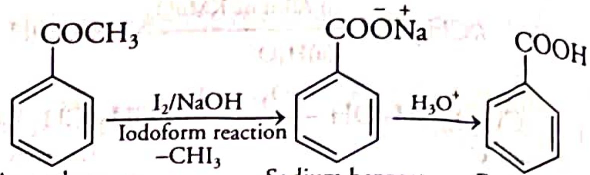
Sol.

(i)



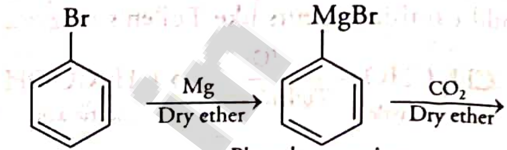
Ethyl benzene   Potassium benzoate   Benzoic acid

(ii)

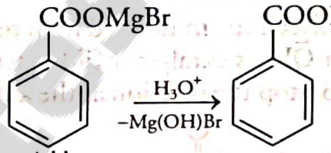


Acetophenone   Sodium benzoate   Benzoic acid

(iii)

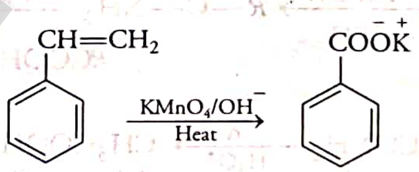


Bromobenzene   Phenyl magnesium bromide

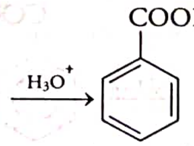


Adduct   Benzoic acid

(iv)



Styrene   Potassium benzoate



Benzoic acid

PHYSICAL PROPERTIES

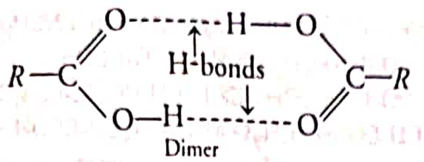
The physical properties of carboxylic acids are described below:

(i) **Physical state** Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours while higher carboxylic acids are wax like solids and odourless due to their low volatility.

(ii) **Solubility** Simple aliphatic carboxylic acids having upto four carbon atoms are miscible with water because of hydrogen bond formation with water. Solubility decreases with increase in the number of carbon atoms which is due to increased hydrophobic interaction of hydrocarbon part. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

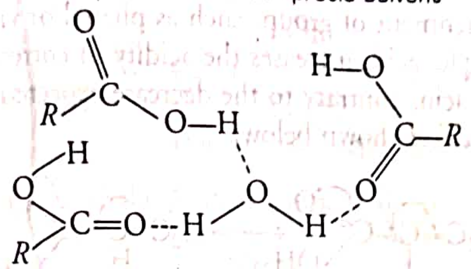
(iii) **Boiling point** As compare to hydrocarbons, aldehydes, ketones and carboxylic acids have higher boiling points because they have high extent of

hydrogen bonding with water, due to which they exists as associated molecules.



Dimer

In vapour state or in aprotic solvent



Hydrogen bonding (dotted) of RCOOH with H_2O

The hydrogen bonds are not broken completely even in the vapour phase. Infact, mostly carboxylic acids exist as dimer in the vapour phase or in aprotic solvent.

(iv) **Melting point** The melting point of aliphatic carboxylic acids do not show a regular pattern rather they show oscillation or alteration effect, i.e. melting point of an acid containing even number of carbon atoms is higher than the next member containing odd number of carbon atoms.

CHEMICAL PROPERTIES

Chemical properties of carboxylic acids are characteristic of carboxyl group and the alkyl or the aryl group. The reactions of carboxylic acids are classified as follows:

Reactions Involving Cleavage of O—H Bond

Acidity

Like alcohols, carboxylic acids also evolve hydrogen with metals and form salts with alkalies similar to phenols. However, unlike phenols, they react with weaker bases like sodium carbonate and hydrogen carbonate to evolve carbon dioxide.

This reaction is used to detect the presence of carboxyl group in an organic compound.

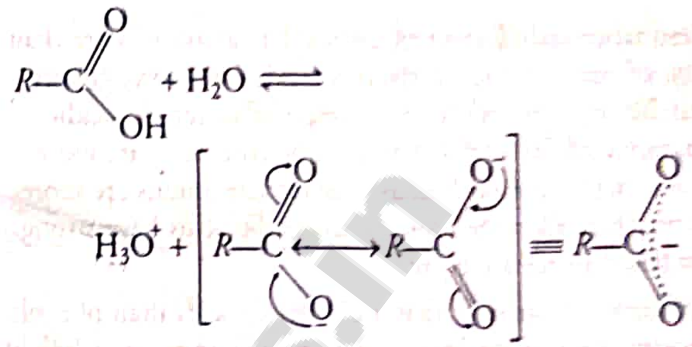
$$2R\text{—COOH} + 2\text{Na} \longrightarrow \underset{\text{Sodium carboxylate}}{2R\text{—CO}\overset{-}{\text{O}}\overset{+}{\text{Na}}} + H_2\uparrow$$

$$R\text{—COOH} + \text{NaOH} \longrightarrow R\text{—CO}\overset{-}{\text{O}}\overset{+}{\text{Na}} + H_2O$$

$$R\text{—COOH} + \text{NaHCO}_3 \longrightarrow R\text{—CO}\overset{-}{\text{O}}\overset{+}{\text{Na}} + H_2O + CO_2\uparrow$$

Reaction in Aqueous Solution

In aqueous solution, carboxylic acids ionise and exist in dynamic equilibrium between the resonance stabilised carboxylate ions and the hydronium ions.



For the above reaction:

$$K_{eq} = \frac{[H_3O^+][RCOO^-]}{[H_2O][RCOOH]};$$

$$K_a = K_{eq}[H_2O] = \frac{[H_3O^+][RCOO^-]}{[RCOOH]}$$

where, K_{eq} is equilibrium constant and K_a is the acid dissociation constant.

The strength of an acid is usually indicated by its pK_a value rather than its K_a value.

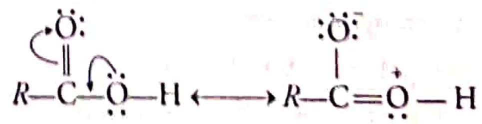
$$pK_a = -\log K_a$$

Smaller the pK_a, stronger is the acid. Strong acids have pK_a values < 1. Trifluoroacetic acid is the strongest organic acid (pK_a of CF_3COOH = 0.23). pK_a of hydrochloric acid, benzoic and acetic acid are –7.0, 4.19 and 4.76, respectively. The acids with pK_a values between 1 and 5 are considered to be moderately strong acids, weak acids have pK_a values between 5 and 15 while extremely weak acids have pK_a values >15.

Carboxylic acids are weaker than mineral acids but they are stronger acids than alcohols (pK_a is ~16 for ethanol) and phenols (pK_a is ~10).

Cause of Acidic Nature of Carboxylic Acids

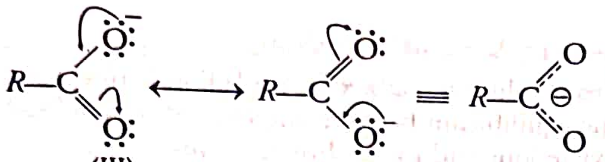
Carboxylic acids may be regarded as a resonance hybrid of the structures I and II.



(I) (II)

Acidic nature of carboxyl group is due to the breaking of O—H bond as positively charged oxygen weakens the bond.

Carboxylate anion formed by the removal of a proton is also stabilised by resonance.


(III) (IV) (V)

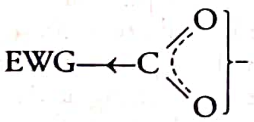
Resonance stabilisation of carboxylate anion is more than that of undissociated carboxylic acid. Therefore, greater stability of carboxylate ion is responsible for the acidic character of carboxylic acids. Carboxylic acids are more acidic than alcohols because carboxylate anions are more stable than alkoxide ions, so carboxylic acids have strong tendency to release a proton.

Similarly, carboxylic acids are stronger acids than phenols because carboxylate ion is much more resonance stabilised than phenoxide ion as negative charge is delocalised over two electronegative O-atoms in carboxylate anion while in phenol, negative charge is delocalised over only one O-atom.

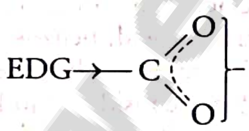
Effect of Substituents on the Acidity of Carboxylic Acids

Substituents may affect the stability of the conjugate base and thus, also affect the acidity of the carboxylic acids.

Electron withdrawing groups (EWGs) increase the stability of the carboxylate ion by dispersing the negative charge through resonance effect on the conjugate base while electron donating groups (EDGs) decrease the stability of the carboxylate ion by intensifying the negative charge.



Acidity of carboxylic acids increases due to the presence of Electron Withdrawing Groups (EWGs)



Acidity of carboxylic acids decreases due to the presence of Electron Donating Groups (EDGs)

The effect of the following substituent groups in the increasing acidity order is

$$Ph < I < Br < Cl < F < CN < NO_2 < CF_3$$

As the $+I$-effect of electron donating group increases, the relative acidic strength decreases as

$$—CH_3 < —C_2H_5 < —CH(CH_3)_2 < — C(CH_3)_3 \text{ (}+I\text{-effect increases)}$$

$$\underset{\text{Acetic acid}}{CH_3COOH} > \underset{\text{Propionic acid}}{CH_3CH_2COOH} >$$

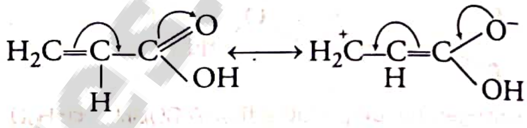
$$\underset{\text{Isobutyric acid}}{(CH_3)_2CHCOOH} > \underset{\text{2,2-dimethylpropanoic acid}}{(CH_3)_3CCOOH}$$

(Relative acidic strength decreases)

Order of Decreasing Acidity of Different Carboxylic Acids Based on pK_a Value

$CF_3COOH > CCl_3COOH > Cl_2CHCOOH > O_2NCH_2COOH > NC\,CH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH > HCOOH > ClCH_2CH_2COOH > C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH > CH_3CH_2COOH$

Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below:

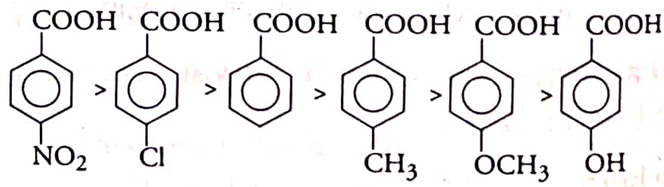


sp^2-hybridised carbon is more electronegative than that of sp^3-hybridised carbon. Therefore, as the hybridisation of carbon atom directly attached to —COOH, changes from $sp^3 \longrightarrow sp^2 \longrightarrow sp$, the acidic strength increases in the order as :

$$\underset{sp^3}{CH_3}COOH < CH_2 = \underset{sp^2}{CH}COOH < \underset{sp^2}{C_6H_5}COOH < HC \equiv \underset{sp}{C} — COOH$$

Benzoic acid is stronger acid than acrylic acid ($CH_2 = CHCOOH$) because delocalisation destroys the aromatic character of the benzene ring.

Acidic strength of few substituted aromatic acids in the decreasing order are:



Reactions Involving Cleavage of C—OH Bond

Esterification

Carboxylic acids react with alcohols or phenols in the presence of a mineral acid such as conc. H_2SO_4 or HCl gas (as a catalyst) to form an ester. This reaction is called esterification.

$$R—COOH + R'—OH \underset{}{\overset{H^+}{\rightleftharpoons}} R—COOR' + H_2O$$

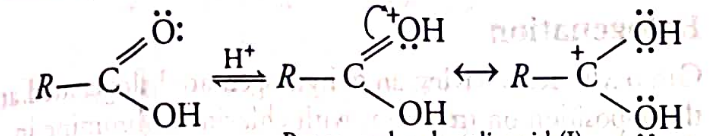
$$\underset{\text{Acetic acid}}{CH_3—COOH} + \underset{\text{Methanol}}{CH_3—OH} \rightleftharpoons \underset{\text{Methyl acetate}}{CH_3—COOCH_3} + H_2O$$

Mechanism

It is a type of nucleophilic acyl substitution reaction that involves majorly three steps:

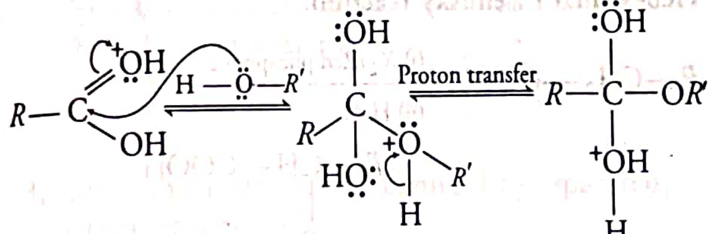
Step 1 : Protonation of the Carbonyl Oxygen

This step activates the carbonyl group towards nucleophilic addition of the alcohol.



Protonated carboxylic acid (I)

Step 2 : Nucleophilic Addition of the Alcohol

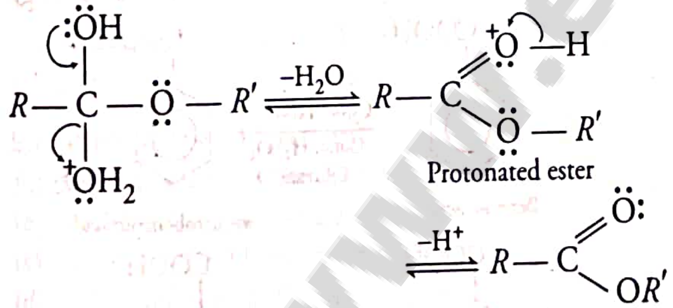


Tetrahedral intermediate

Proton transfer in the tetrahedral intermediate converts the hydroxyl group into $-\overset{+}{O}H_2$ group.

Step 3 : Loss of Water Molecule and a Proton

The $-\overset{+}{O}H_2$ group being better leaving group is eliminated as neutral water molecule. The protonated ester so formed finally loses a proton to give the ester.

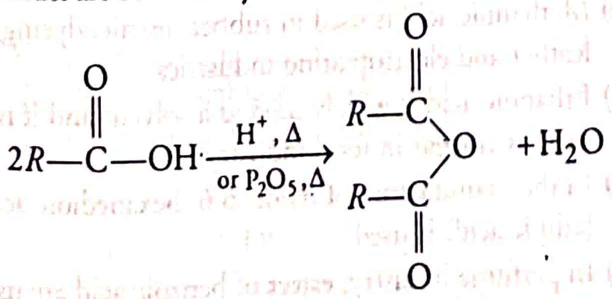


Protonated ester

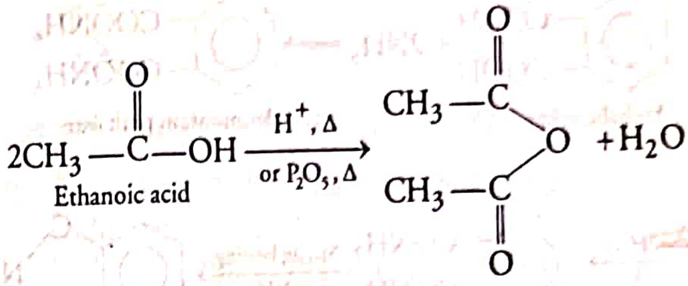
Ester

Anhydride Formation

Carboxylic acids on heating with mineral acids such as H_2SO_4 or with P_2O_5 give corresponding anhydride. Acid anhydrides are obtained by the elimination of water molecule.



Acid anhydride



Ethanoic acid

Ethanoic anhydride

Reactions with Phosphorus Trihalides, Phosphorus Pentahalides and Thionyl Chloride

The hydroxyl group of carboxylic acids behaves like that of alcohols and is easily replaced by chlorine atom on treating with PCl_5, PCl_3 or $SOCl_2$.

$$R\text{—}COOH + PCl_5 \longrightarrow \underset{\text{Acyl chloride}}{RCOCl} + POCl_3 + HCl$$

$$3RCOOH + PCl_3 \longrightarrow 3R\text{—}COCl + H_3PO_3$$

$$R\text{—}COOH + SOCl_2 \longrightarrow R\text{—}COCl + SO_2\uparrow + HCl\uparrow$$

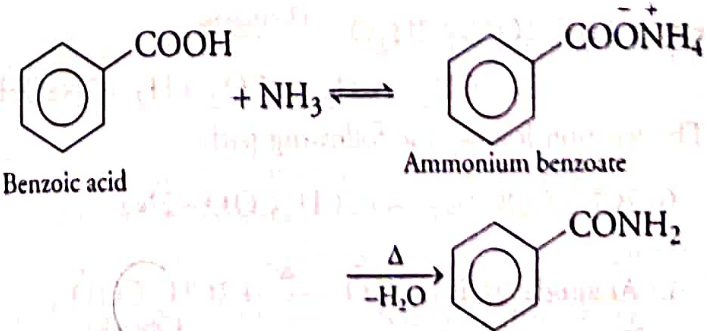
Note Thionyl chloride ($SOCl_2$) reagent is preferred to carry out reaction because the other two products obtained are gaseous and escape the reaction mixture making the purification of products easier.

Reaction with Ammonia

Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature give amides.

$$R\text{—}COOH + NH_3 \rightleftharpoons \underset{\text{Ammonium salt}}{R\text{—}COO^-NH_4^+} \xrightarrow[\Delta]{-H_2O} \underset{\text{Acid amide}}{R\text{—}CONH_2}$$

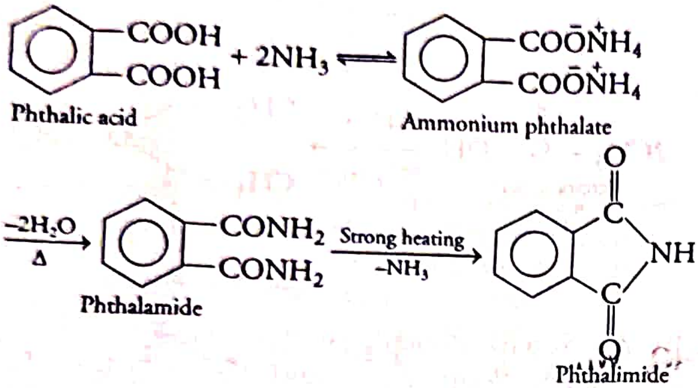
$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \rightleftharpoons \underset{\text{Ammonium acetate}}{CH_3CO\overset{-}{O}\overset{+}{N}H_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$



Benzoic acid

Ammonium benzoate

Benzamide



Reactions Involving —COOH Group

Reduction

Carboxylic acids are reduced to primary alcohols by $LiAlH_4$ and more easily with diborane.

$$R\text{—}COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4/\text{Ether or } B_2H_6} R\text{—}CH_2OH$$

Diborane does not easily reduce functional groups such as ester, nitro, halo, etc.

$NaBH_4$ does not reduce the carboxyl group.

Decarboxylation

The loss of CO_2 molecule from a carboxylic acid to form hydrocarbons is called decarboxylation.

(i) **Using soda lime** Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with soda lime (NaOH and CaO in the ratio of 3 : 1).

$$R\text{—}CO\overset{-}{O}\overset{+}{Na} \xrightarrow[\text{Heat}]{\text{NaOH and CaO}} \underset{\text{Alkane}}{R\text{—}H} + Na_2CO_3$$

(ii) **Electrolytic decarboxylation** (Kolbe electrolysis)

Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of acid. This reaction is known as **Kolbe electrolysis**.

e.g. $2CH_3CO\overset{-}{O}\overset{+}{Na} + 2H_2O \xrightarrow{\text{Electrolysis}}$

$$CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

The reaction follows the following path:

(i) $2CH_3COONa \longrightarrow 2CH_3CO\overset{-}{O} + 2\overset{+}{Na}$

(ii) At anode $2CH_3CO\overset{-}{O} \xrightarrow{-2e^-} \underset{\text{(Unstable)}}{2CH_3CO\dot{O}:}$

$$\longrightarrow \underset{\text{Alkane}}{2\dot{C}H_3} + 2CO_2\uparrow$$

(iii) $\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3\uparrow$

(iv) At cathode $H_2O^{\bullet} + e^- \longrightarrow OH^- + \dot{H}$

$$2\dot{H} \longrightarrow H_2\uparrow$$

Substitution Reactions in the Hydrocarbon Part

Halogenation

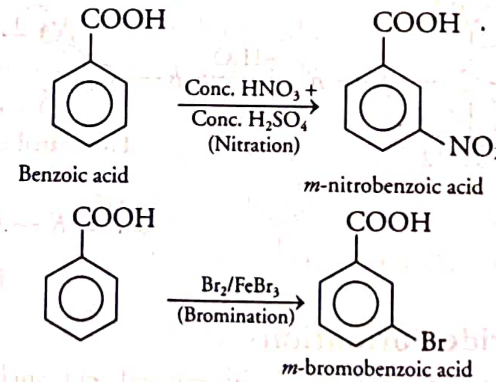
Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. This reaction is known as **Hell-Volhard-Zelinsky reaction.**

$$R\text{—}CH_2\text{—}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red phosphorus}} \underset{\alpha\text{-halocarboxylic acid}}{R\text{—}\underset{X}{\underset{|}{C}H}\text{—}COOH}$$

(where, X = Cl, Br)

Ring Substitution Reaction

Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and *meta*-directing group. However, they do not undergo Friedel-Crafts reaction because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.



Uses

Some important uses of carboxylic acids are as follows:

(i) Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries.

(ii) Ethanoic acid is widely used as a solvent and it is also used as vinegar in food industry.

(iii) In the manufacture of nylon-6,6, hexanedioic acid (adipic acid) is used.

(iv) In perfume industry, esters of benzoic acid are used.

(v) Sodium benzoate is used as a food preservative.

(vi) Higher fatty acids are extremely useful in production of soaps and detergents.

TOPIC PRACTICE 2

OBJECTIVE Type Questions

1. IUPAC name of α-acetyl succinic acid is
   (a) 2-(1-oxoethyl) butane-1,4-dioic acid
   (b) 3-(2-oxoethyl) butane-1,4-dioic acid
   (c) Hexan-1,6-dioic acid
   (d) Butane-1,4-dicarboxylic acid

2. Select the reagent for the given conversion.
   $CH_3(CH_2)_8CH_2OH \longrightarrow CH_3(CH_2)_8COOH$
   (a) $KMnO_4$ in acidic, neutral, alkaline media
   (b) $K_2Cr_2O_7$ in acidic media
   (c) CrO_3 in acidic media
   (d) All of the above

3. Select the acid(s) which cannot be prepared by Grignard reagent?
   (a) Acetic acid (b) Succinic acid
   (c) Formic acid (d) All of these

4. Which of the following is the strongest acid?
   (a) CH_3COOH (b) $ClCH_2COOH$
   (c) $Cl_2CHCOOH$ (d) $Cl_3C—COOH$

5. Which of the following reagents is/are used for the conversion of ethanoic acid to ethanoic anhydride?
   (a) $SOCl_2, \Delta$ (b) PCl_3, Δ
   (c) P_2O_5, Δ (d) All of these

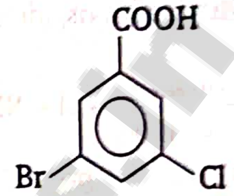
6. Sodalime is the mixture of
   (a) NaOH and CaO in the ratio of 3 : 2
   (b) NaOH and CaO in the ratio of 1 : 3
   (c) NaOH and CaO in the ratio of 3 : 1
   (d) NaOH and CaO in the ratio of 2 : 3

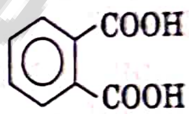
7. What is the by-product formed in this reaction
   $$R—COONa \xrightarrow[\Delta]{NaOH,\ CaO} R—H + ?$$
   (a) $NaHCO_3$ (b) CO_2
   (c) Na_2HCO_3 (d) Na_2CO_3

8. The product formed during Hell-Volhard-Zelinsky reaction is
   (a) $R—\underset{\substack{|\\ X}}{CH}—COOH$ (b) $R—CH_2—COX$
   (c) $R—\overset{\substack{X\\ |}}{\underset{\substack{|\\ X}}{C}}—COOH$ (d) $R—\underset{\substack{|\\ X}}{CH}—CH_2—COOH$

VERY SHORT ANSWER Type Questions

9. Write the IUPAC name of the following compound:
   $$CH_3—\underset{\substack{|\\ OH}}{CH}—CH_2—COOH$$
   All India 2014

10. Write the IUPAC name of
    
    All India 2011C

11. Write the IUPAC and common name of
    

12. Draw the structure of 2-hydroxybenzoic acid.
    Delhi 2014

13. Draw the structural formula of hex-2-en-5-ynoic acid.

14. What happens when methylbenzene is oxidised with alkaline $KMnO_4$? All India 2014

15. Arrange the following compounds in the increasing order of their property as indicated.
    $Cl—CH_2—COOH, F—CH_2—COOH,$
    $CH_3—COOH$ (acidic character)
    NCERT Exemplar; All India 2015

16. Arrange the following compounds in the increasing order of their acidic strength.
    $(CH_3)_3CCOOH,\ CH_3CH_2\underset{\substack{|\\ Br}}{CH}—COOH,$
    $(CH_3)_2CHCOOH, CH_3—\underset{\substack{|\\ Br}}{CH}—CH_2COOH$

17. Give simple chemical tests to distinguish between the following pair of compounds.
    Benzoic acid and phenol. Delhi 2013

18. Write the reagents required in the following reaction: $CH_3—COOH \xrightarrow{?} CH_3—CONH_2$
    All India 2015

19. Name the reagents used in the following reaction.

$$C_6H_5-CH_2-CH_3 \xrightarrow{?} C_6H_5-COO^-K^+$$ **Delhi 2015**

20. Predict the product of the following reaction:

$$CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} ?$$ **Delhi 2015**

21. Complete the following reaction:

$$CH_3COOH \xrightarrow{Br_2/P}$$ **Delhi 2013**

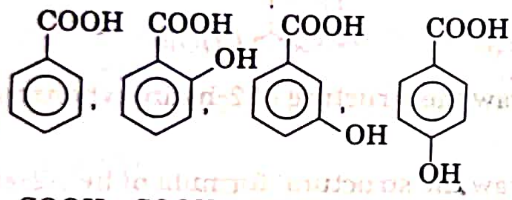
SHORT ANSWER Type I Questions

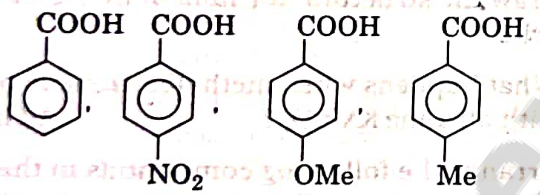
22. In the following reactions, identify the compounds A and B.

(i) $R-CN \xrightarrow[H^+/H_2O/\Delta]{\text{Hydrolysis}} A + NH_3$

(ii) $A + SOCl_2 \longrightarrow B + SO_2\uparrow + HCl\uparrow$

23. Give the decreasing order of acidic character of the following compounds:

(i) 

(ii) 

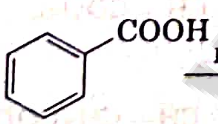
24. How will you convert the following?

(i) Ethanal to 2-hydroxy propanoic acid

(ii) Toluene to benzoic acid **All India 2013**

25. Predict the products of the following reactions:

(i) $C_6H_5-CH_3 \xrightarrow[\text{(ii) } H^+]{\text{(i) } KMnO_4/\ KOH} ?$

(ii)  $\xrightarrow{Br_2/FeBr_3} ?$

All India 2015

26. Arrange the following compounds in the increasing order of their property as indicated.

(i) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acidic strength).

(ii) Benzoic acid, 4-nitrobenzoic acid, 3,4-dinitro benzoic acid, 4-methoxy benzoic acid (acidic strength). **NCERT**

Presence of electron withdrawing group, (EWG) makes an acid more acidic. As the distance between EWG and — COOH group increases, acidity decreases.
As the distance between –*I*-effect showing group and —COOH group increases, acidity decreases.

27. How do you convert the following?

(a) Ethanal to propanone

(b) Toluene to benzoic acid

Or Account for the following:

(a) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.

(b) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid. **CBSE 2018**

28. Compound A was prepared by the oxidation of compound B with alkaline $KMnO_4$. Compound A on reduction with lithium aluminium hydride gets converted back to compound B. When compound A is heated with compound B in the presence of H_2SO_4, it produces fruity smell of compound C. To which family, the compounds A, B and C belongs to? **NCERT Exemplar**

Presence of electron withdrawing group (EWG) makes an acid more acidic. As the distance between EWG and (—COOH) group increases, acidity decreases.

29. Arrange the following in the increasing order of their property indicated. (Any two) **CBSE SQP (Term-II)**

(i) Benzoic acid, phenol, picric acid, salicylic acid (pK_a values).

(ii) Acetaldehyde, acetone, methyl *tert*-butylketone (reactivity towards NH_2OH).

(iii) Ethanol, ethanoic acid, benzoic acid (boiling point).

SHORT ANSWER Type II Questions

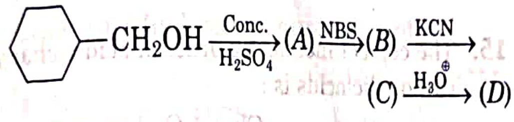
30. Identify the compounds A, B and C in the following reaction.

$$CH_3-Br \xrightarrow{Mg\ /\ Ether} [A] \xrightarrow[\text{(ii) Water}]{\text{(i) } CO_2} [B] \xrightarrow{CH_3OH\ /\ H^+} [C]$$

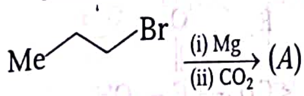
NCERT Exemplar

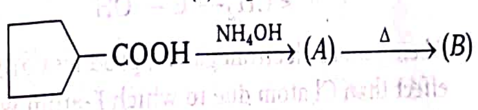
31. Account for the following.
(i) $Cl-CH_2COOH$ is a stronger acid than CH_3COOH.
(ii) Carboxylic acids do not give reactions of carbonyl group. **Delhi 2014**

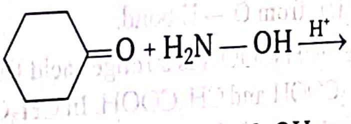
LONG ANSWER Type Questions

32. Complete the following reactions:
(i) 

(ii) $\begin{array}{l}COOH\\ |\\ COOH\end{array} + NH_3 \xrightarrow{\Delta} (A)$

(iii) 

(iv) 

33. (i) Write the products of the following reactions:
(a) 

(b) $2C_6H_5CHO + \text{conc. } NaOH \longrightarrow$
(c) $CH_3COOH \xrightarrow{Cl_2/P}$
(ii) Give simple chemical tests to distinguish between the following pairs of compounds.
(a) Benzaldehyde and benzoic acid.
(b) Propanal and propanone **All India 2020, 2014**

34. Give the simple chemical tests to distinguish between the following pairs of compounds.
(i) Acetophenone and benzophenone
(ii) Phenol and benzoic acid
(iii) Benzoic acid and ethyl benzoate
(iv) Pentan-2-one and pentan-3-one **NCERT**
(v) Ethanal and propanal

35. (i) Account for the following:
(a) Electrophilic substitution in benzoic acid takes place at *meta* position.
(b) Carboxylic acids do not give characteristic reactions of carbonyl group.
(ii) Give simple chemical test to distinguish between the following pairs of compounds:
(a) Acetophenone and benzaldehyde
(b) Benzoic acid and ethylbenzoate

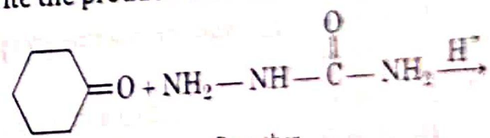
Or

(i) Write structures of *A*, *B*, *C* and *D* in the following reaction sequence:

$$CH_3COCl \xrightarrow{H_2/Pd\text{-}BaSO_4} A \xrightarrow{\text{Dil. NaOH}} B \xrightarrow{\Delta} C \xrightarrow{CH_3MgBr/H_3O^+} D$$

(ii) Arrange the following compounds in the increasing order of their boiling points:
CH_3CHO, CH_3CH_2OH, CH_3OCH_3, CH_3COOH **All India 2017C**

36. (i) How will you convert
(a) benzene to acetophenone?
(b) propanone to 2-methylpropan-2-ol?
(ii) Give reasons
(a) Electrophilic substitution in benzoic acid takes place at *meta* position.
(b) Carboxylic acids are higher boiling liquids than aldehydes, ketones and alcohols of comparable molecular masses.

Or (i) Write the products of the following reactions:
(a) 

(b) $CH_3MgBr + CO_2 \xrightarrow[H_3O^+]{\text{Dry ether}}$
(c) $CH_3CH_2COOH + Br_2 \xrightarrow{\text{Red phosphorus}}$
(ii) Write a simple chemical test to distinguish between the following pairs of compounds.
(a) Propanal and propanone
(b) Benzaldehyde and Benzoic acid **Delhi 2017C**

37. An organic compound 'A' C_8H_6 on treatment with dilute H_2SO_4 containing mercuric sulphate gives compound 'B'. This compound 'B' can also be obtained from a reaction of benzene with acetyl chloride in presence of anhy. $AlCl_3$. 'B' on treatment with I_2 in aq. KOH gives 'C' and a yellow compound 'D'. Identify A, B, C and D. Give the chemical reactions involved. **CBSE SQP 2021**

38. (i) Write the reaction for cross aldol condensation of acetone and ethanal. **CBSE SQP 2021**
(ii) How will you carry out the following conversions
(a) Benzyl alcohol to phenyl ethanoic acid
(b) Propanone to propene
(c) Benzene to m-nitroacetophenone

HINTS AND EXPLANATIONS

1. (a) $\underset{4}{HOOC}-\underset{\underset{(\beta)}{3}}{CH_2}-\underset{\underset{(\alpha)}{2}}{\overset{\overset{1}{COCH_3}}{\overset{|}{CH}}}-\underset{1}{COOH}$

   Common name → α-acetyl succinic acid.
   IUPAC name → 2- (1-oxoethyl) butane-1, 4-dioic acid.

2. (d) Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as $KMnO_4$ in neutral, acidic or alkaline medium or by $K_2Cr_2O_7$ and CrO_3 in acidic medium.

   $$CH_3(CH_2)_8CH_2OH \xrightarrow[\text{or } CrO_3\text{-}H_2SO_4]{\text{Alk. } KMnO_4,\ H_3O^+} CH_3(CH_2)_8COOH$$

3. (c) Formic acid cannot be prepared by Grignard reagent because it is a step up process i.e. used to synthesise carboxylic acids having one carbon atom more than that present in reactant. As formic acid (HCOOH) contain one carbon atom. So, it cannot be synthesised by this method.

4. (d) $Cl_3C-COOH$ is the strongest acid due to presence of three electron withdrawing chlorine group (Cl_3), next to $-COOH$ group.

5. (c) Carboxylic acids on heating with mineral acids such as H_2SO_4 or P_2O_5 give corresponding anhydride.

6. (c) Soda lime is a mixture of NaOH and CaO in the ratio of 3 : 1. This is used as reagent in decarboxylation reaction.

   $$RCO\overset{-}{O}\overset{+}{Na} \xrightarrow[\Delta]{\text{NaOH and CaO}} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

7. (d) Na_2CO_3 is the by product formed in the given reaction.

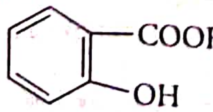
   $$R-CO\overset{-}{O}\overset{+}{Na} \xrightarrow[\text{CaO, heat}]{\text{NaOH and}} RH + Na_2CO_3$$

8. (a) Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.

9. 3-hydroxybutanoic acid

10. 3-bromo-5-chlorobenzoic acid

11. **Common Name** Phthalic acid
    IUPAC Name Benzene-1, 2-dicarboxylic acid

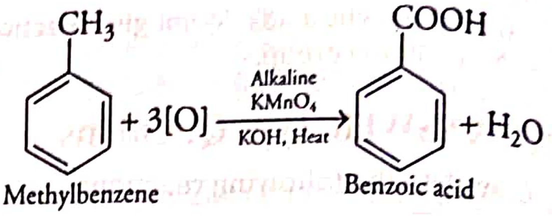
12. 

    2-hydroxybenzoic acid

13. $HC\equiv C-CH_2-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-COOH$

    Hex -2-en -5-ynoic acid

14. Benzoic acid is obtained.



15. The correct increasing order of acidic character of carboxylic acids is :

    $$CH_3-\overset{\overset{O}{\|}}{C}-OH < \overset{\overset{Cl}{|}}{CH_2}-\overset{\overset{O}{\|}}{C}-OH < \overset{\overset{F}{|}}{CH_2}-\overset{\overset{O}{\|}}{C}-OH$$

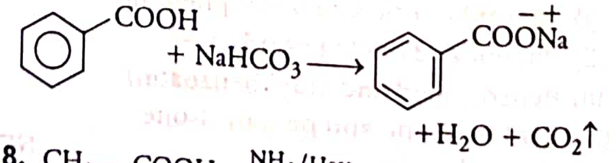
    F being more electronegative, produces greater $-I$-effect than Cl atom due to which F-atom withdraws electron from $O-H$ bond and thereby making $O-H$ bond weaker and hence, facilitates the release of H^+ ion from $O-H$ bond.

    Hence, FCH_2COOH is stronger acid than $ClCH_2COOH$ and CH_3COOH. In CH_3COOH, due to $+I$-effect of methyl group, electron density in $O-H$ bond increases.

    As a result, release of H^+ ions from acetic acid becomes more difficult.

16. $CH_3CH_2\underset{\underset{Br}{|}}{CH}COOH > CH_3\underset{\underset{Br}{|}}{CH}CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$

17. **Benzoic acid and phenol** Benzoic acid reacts with sodium bicarbonate to produce effervescence of carbon dioxide whereas phenol does not.



    $+H_2O + CO_2\uparrow$

18. $CH_3-COOH \xrightarrow[-H_2O]{NH_3/\text{Heat}} CH_3-CONH_2$

19. $C_6H_5-CH_2-CH_3 \xrightarrow{KMnO_4\text{-}KOH} C_6H_5-CO\overset{-}{O}K^+$

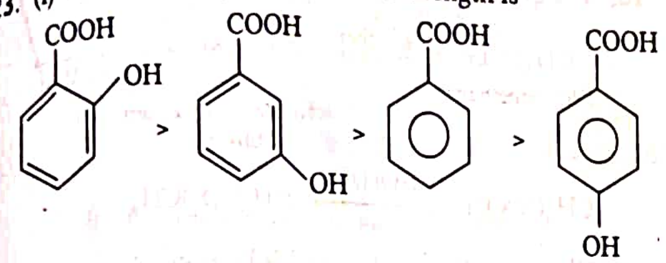
20. $CH_3CO\overset{-}{O}\overset{+}{Na} \xrightarrow[\Delta]{NaOH/CaO} CH_3-H + Na_2CO_3$

21. $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Br_2/P} \underset{\underset{Br}{|}}{CH_2}-COOH$

    α-bromoacetic acid

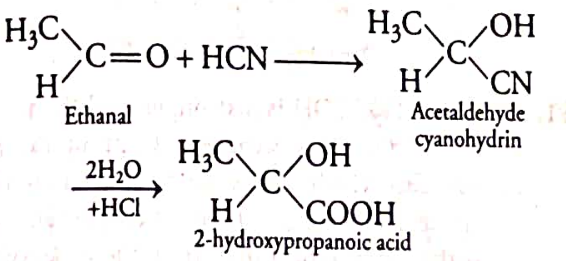
22. (i) $A = RCOOH$
    (ii) $A = RCOOH,\ B = RCOCl$

23. (i) The decreasing order of acidic strength is

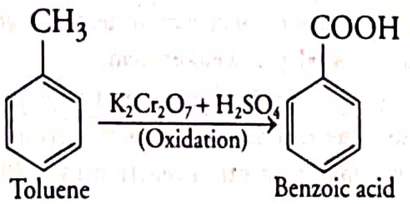


(ii) Refer to text on page 340.

24. (i) **Ethanal to 2-hydroxy propanoic acid**

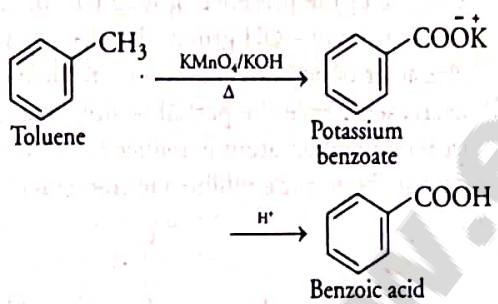


(ii) **Toluene to benzoic acid**

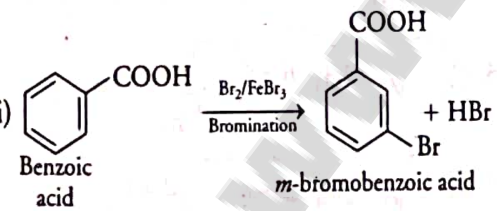


25.

(i)



(ii)



26. (i) As $+I$- effect of isopropyl group is more than that of n-propyl group, therefore, $(CH_3)_2CHCOOH$ is a weaker acid than $CH_3CH_2CH_2COOH$. Since, $-I$- effect decreases with distance, therefore, $CH_3CH_2CH(Br)COOH$ is a stronger acid than $CH_3CH_2CH(Br)CH_2COOH$.

Hence, increasing order of acidic strength is:

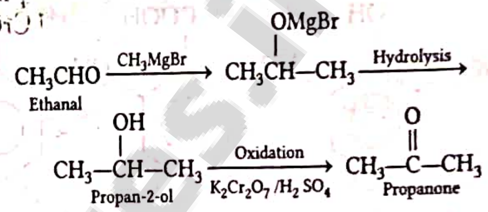
$(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH$
$< CH_3CH(Br)CH_2COOH$
$< CH_3CH_2CH(Br)COOH$

(ii) Electron donating group ($—OCH_3$) decreases the acidic strength therefore, 4-methoxy benzoic acid is a weaker acid than benzoic acid whereas electron withdrawing group ($—NO_2$) increases the same therefore, both 4-nitrobenzoic acid and 3,4-dinitrobenzoic acid are stronger acids than benzoic acid. Further, due to the presence of an additional $—NO_2$ group at m-position with respect to COOH group, 3,4-dinitrobenzoic acid is a little stronger acid than 4-nitrobenzoic acid.

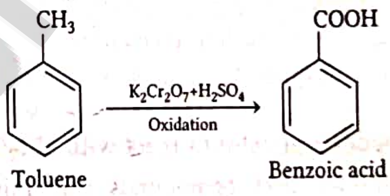
Hence, increasing order of acidic strength is

4-methoxy benzoic acid < benzoic acid < 4-nitrobenzoic acid < 3,4-dinitrobenzoic acid.

27. (a) **Ethanal to propanone**



(b) **Toluene to benzoic acid**



Or

(a) The —COOH group attached to benzene ring is electron withdrawing in nature and thus deactivates Ring. Secondly, the catalyst used in the reaction, i.e. $AlCl_3$ is a Lewis acid which has the tendency to bonded to carboxyl group.

That's why aromatic carboxylic acid does not undergo Friedel Craft's reaction.

(b) Lower pK_a value means stronger acid. pK_a value of 4-nitro benzoic acid is lower than benzoic acid due to following reasons:

(i) Due to $-I$ and $-R$ effect of $—NO_2$ group, electron density in O—H bond decreases, thus it becomes weak and easily loses a proton and therefore it is more acidic.

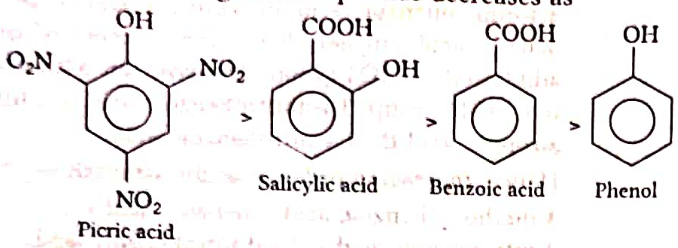
(ii) Due to $-I$ and $-R$ effect of $—NO_2$ group, delocalisation of – ve charge occurs and p-nitrobenzoate ion becomes more stable than benzoate ion.

28. $\underset{\text{Alcohol}}{\underset{(B)}{RCH_2OH}} \xrightarrow[\text{[O]}]{\text{Alkaline } KMnO_4} \underset{\text{Carboxylic acid}}{\underset{(A)}{R\,COOH}}$

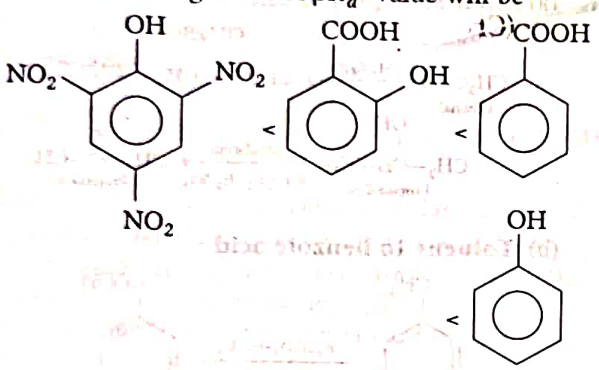
$\underset{(A)}{\underset{\text{Carboxylic acid}}{R\,COOH}} \xrightarrow{LiAlH_4} \underset{(B)}{\underset{\text{Alcohol}}{R\,CH_2\,OH}}$

$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{RCH_2OH} \underset{\Delta}{\overset{H_2SO_4}{\rightleftharpoons}} \underset{\text{(Fruity smell)}}{\underset{(C)}{\underset{\text{Ester}}{RCOOCH_2R}}} + H_2O$

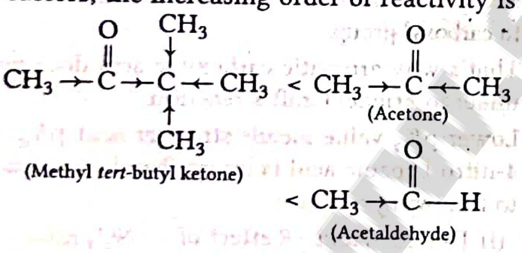
29. (i) Weaker is the acid means higher is the pK_a value. The acidity of the given compounds decreases as



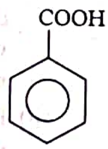
Thus, increasing order of pK_a value will be



(ii) Aldehydes and ketones react with NH_2OH in weakly medium to form compounds containing $\rangle C=N$ group. The order of reactivity decreases with increase in $+I$-effect of alkyl group. It also decreases with increase in steric hindrance due to the size as well as number of alkyl groups. On considering these two factors, the increasing order of reactivity is



(iii) CH_3CH_2OH Ethanol (Molar mass =46.0) I; CH_3COOH Ethanoic acid (Molecular mass = 60) II;



Benzoic acid (Molecular mass = 122) III

Boiling point of carboxylic acids is higher than alcohols because they have high extent of H-bonding with water, due to which they exists as associated molecules. Thus, II and III have higher boiling point than I. Also boiling point increase with increase in molar mass.

Thus, boiling point of III is higher than II. Therefore, the increasing order is I < II < III.

30. Complete chemical conversion can be done as:

$$\underset{\text{Bromomethane}}{CH_3-Br} \xrightarrow{Mg/Ether} \underset{\substack{[A]\\ \text{Methyl magnesium bromide}}}{CH_3MgBr} \xrightarrow[\text{(ii) Water}]{\text{(i) } CO_2}$$

$$\underset{\substack{(B)\\ \text{Ethanoic acid}}}{CH_3COOH} \xrightarrow{CH_3OH/H^+} \underset{\substack{(C)\\ \text{Methyl ethanoate}}}{CH_3COOCH_3}$$

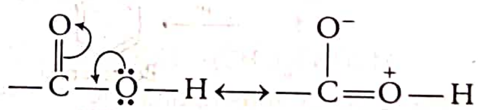
Hence, $A = CH_3MgBr$, $B = CH_3COOH$,

$$C = CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3$$

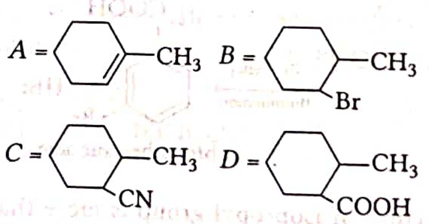
31. (i) $Cl-CH_2COOH$ is a stronger acid than CH_3COOH. It is because $-Cl$ group exhibits $-I$-effect which makes the carboxylate ion more stable. Higher the stability of carboxylate ion, easier is the removal of proton from the carboxylic acid and stronger is the acid. In CH_3COOH, $-CH_3$ group has $+I$-effect which destabilised it. Hence, CH_3COOH is a weaker acid.

(ii) Carboxylic acids contain carbonyl group but do not show the reactions of carbonyl group such as nucleophilic addition reaction like aldehydes and ketones.

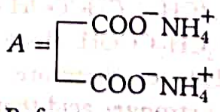
Because of the presence of lone pair of electrons on the O-atom of –OH group, the electrophilic character of carbonyl carbon by resonance decreases, hence the partial positive charge on carbonyl carbon atom is reduced and therefore, they do not show nucleophilic addition reactions.



32. (i)

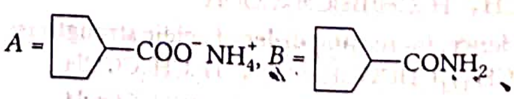


(ii)



(iii) Refer to text on page 338.

(iv)



33. (i) (a) Refer to text on page 317 example 2 (i).

(b) Refer to text on page 321.

(c) $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Cl_2/P} \underset{\text{Monochloroacetic acid}}{ClCH_2COOH}$

$\xrightarrow{Cl_2/P} \underset{\text{Dichloroacetic acid}}{Cl_2CHCOOH} \xrightarrow{Cl_2/P} \underset{\text{Trichloroacetic acid}}{Cl_3CCOOH}$

(ii) (a) **Benzaldehyde and benzoic acid**

$NaHCO_3$ test Benzoic acid being an acid reacts with $NaHCO_3$ solution, to produce brisk effervescence due to evolution of CO_2 while benzaldehyde does not give this test.

$C_6H_5COOH + NaHCO_3 \longrightarrow$

$C_6H_5CO\overset{-}{O}\overset{+}{Na} + CO_2\uparrow + H_2O$

$C_6H_5CHO \xrightarrow{NaHCO_3 \text{ solution}} \text{No effervescence}$

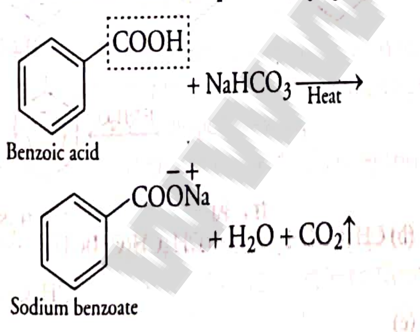
(b) **Propanal and propanone** Propanone responds to iodoform test whereas propanal (CH_3CH_2CHO), does not due to the absence of $CH_3CO—$ group.

$\underset{\text{Propanone}}{CH_3COCH_3} + \underset{\substack{\text{Sodium}\\\text{hypoiodite}}}{3NaOI} \xrightarrow[\text{Heat}]{NaOH, I_2}$

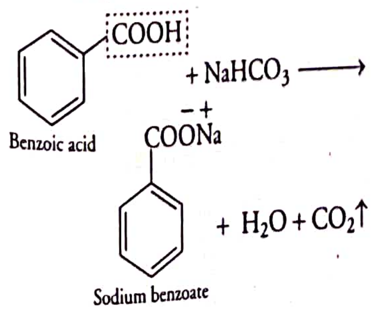
$\underset{\substack{\text{(Yellow ppt.)}\\\text{Iodoform}}}{CHI_3\downarrow} + \underset{\substack{\text{Sodium}\\\text{acetate}}}{CH_3CO\overset{-}{O}\overset{+}{Na}} + 2NaOH$

34. (i) **Acetophenone and benzophenone** Acetophenone ($C_6H_5COCH_3$) gives positive iodoform test whereas benzophenone ($C_6H_5COC_6H_5$) does not.

(ii) **Phenol and benzoic acid** Benzoic acid reacts with sodium bicarbonate to produce effervescence of carbon dioxide whereas phenol (C_6H_5OH) does not.



(iii) **Benzoic acid and ethyl benzoate** Benzoic acid reacts with sodium bicarbonate to produce effervescence of carbon dioxide whereas ethyl benzoate ($C_6H_5COOC_2H_5$) does not.



(iv) **Pentan-2-one and pentan-3-one** *Pentan-2-one responds positively towards iodoform test whereas pentan-3-one ($C_2H_5COC_2H_5$) does not.*

$\underset{\text{Pentan-2-one}}{CH_3—CO—CH_2—CH_2—CH_3} + 3NaOI$

$\xrightarrow{\text{Heat}} \underset{\text{(Yellow ppt.)}}{CHI_3\downarrow} + CH_3CH_2CH_2CO\overset{-}{O}\overset{+}{Na} + 2NaOH$

(v) **Ethanal and propanal** Ethanal responds positively towards iodoform test whereas propanal (CH_3CH_2CHO) does not.

$\underset{\text{Ethanal}}{CH_3CHO} + 3NaOI \xrightarrow{\text{Heat}} \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3\downarrow} + HCO\overset{-}{O}\overset{+}{Na} + 2NaOH$

35. (i) (a) Electrophilic substitution in benzoic acid takes places at *meta* position because carboxylic group is a deactivating group. The presence of electron withdrawing carboxylic group results in a decreased electron density at *o*-and *p*-position.

(b) Due to resonance, electrophilicity of carbonyl carbon is reduced.

(ii) (a) Add NaOH and I_2 to both the compounds and heat them. Acetophenone forms yellow precipitate of iodoform while benzaldehyde does not.

(b) Add $NaHCO_3$ solution to both the compounds. Benzoic acid will give effervescence and liberate CO_2 while ethylbenzoate does not.

Or

(i) $CH_3COCl \xrightarrow{H_2/Pd\text{-}BaSO_4} \underset{(A)}{CH_3CHO} \xrightarrow{\text{Dil. NaOH}}$

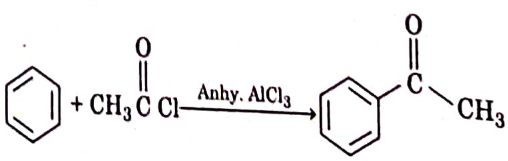
$CH_3CHO \xrightarrow{CH_3MgBr/H_3O^+} \underset{(D)}{CH_3—CH(CH_3)—OH}$

$\xrightarrow{\text{Dil. NaOH}} \underset{(B)}{CH_3—CH(OH)—CH_2CHO} \xrightarrow{\Delta} \underset{(C)}{CH_3—CH{=}CHCHO}$

(ii) The correct increasing order of the boiling points is :

$CH_3—O—CH_3 < CH_3CHO < CH_3CH_2OH < CH_3COOH$

36. (i) (a) **Benzene to acetophenone**



(b) Propanone to 2-methylpropan-2-ol

$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + CH_3MgX \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OMgX$$

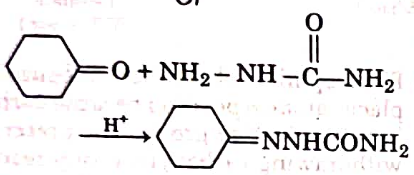
$$\xrightarrow{H_2O} CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

(ii) (a) Refer to solution 36 (i) (a).

(b) Due to extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.

Or

(i) (a)



(b) $CH_3MgBr + CO_2 \xrightarrow[H_3O^+]{\text{Dry ether}} CH_3COOH$

(c) $CH_3CH_2COOH + Br_2 \xrightarrow{\text{Red phosphorus}} CH_3-\underset{Br}{\underset{|}{CH}}-COOH$

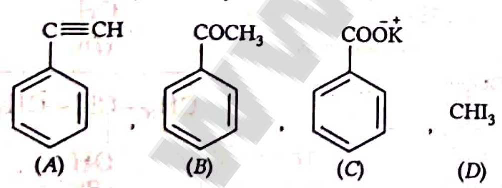
(ii) (a) **Propanal and propanone**

Add ammoniacal solution of silver nitrate or Tollen's reagent to both the compounds, propanal will give silver mirror while propanone does not.

(b) **Benzaldehyde and benzoic acid**

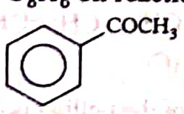
Add $NaHCO_3$ solution to both the compounds, benzoic acid will give effervescence and liberate CO_2, while benzaldehyde will not.

37. *A*, *B*, *C* and *D* respectively are

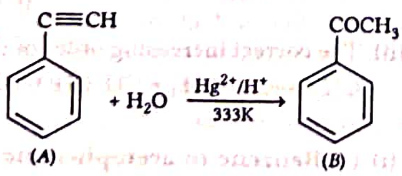


Complete reactions are as follows :

- C_8H_6 on reaction with dil. H_2SO_4, $HgSO_4$ gives

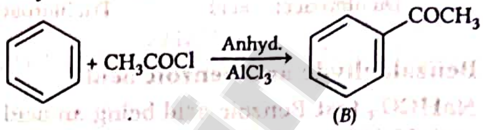


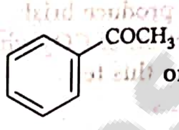
(B)



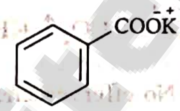
- $C_6H_5COCH_3$ (*B*) can also be obtained from benzene with acetyl chloride in presence of anhyd. $AlCl_3$.

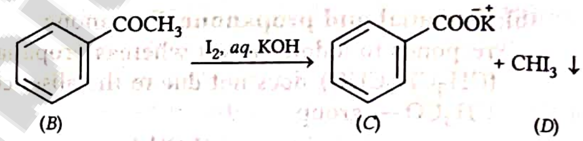
This reaction is known as Friedel-Craft acetylation reaction.





on treatment with I_2 in *aq.* KOH gives



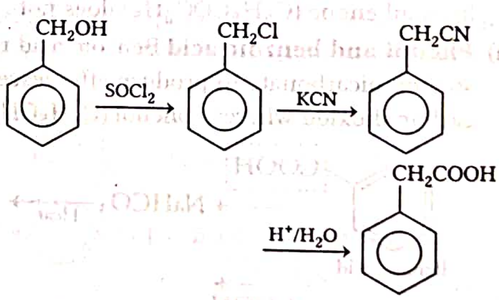


38. (i) Cross-aldol reaction is carried out between two different aldehydes or ketones (acetone and ethanal). It gives a mixture of two products.

$$CH_3COCH_3 + CH_3CHO \xrightarrow{\text{Dil. NaOH}} (CH_3)_2C(OH)CH_2CHO + CH_3CH(OH)CH_2COCH_3$$

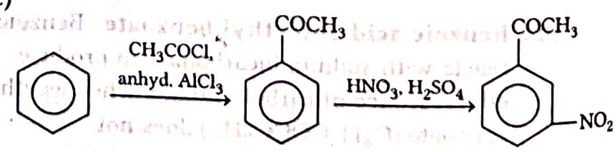
$$\xrightarrow{\text{Heat}} (CH_3)_2C = CHCHO + CH_3CH = CHCOCH_3$$

(ii) (a)



(b) $CH_3COCH_3 \xrightarrow{H_2 \cdot Pd} CH_3CH(OH)CH_3 \xrightarrow{H_2SO_4} CH_3CH = CH_2$

(c)



SUMMARY

- **Aldehyde and Ketones**
  - Carbonyl compounds are sp^2 hybridised containing $-\overset{\overset{\displaystyle O}{\|}}{C}-$ functional group and are classified into aldehydes and ketones.
  - Carbonyl compounds show chain isomerism, position isomerism, functional isomerism and metamerism.

Preparation

(a) **Common methods for the preparation of both aldehydes and ketones are :**
- Oxidation of alcohol
- Catalytic dehydrogenation
- Ozonolysis

(b) **Preparation of only aldehydes**
- Reduction of acid chlorides and ester.
- Reduction of nitriles
- Reduction of methylbenzene
- Side chain chlorination followed by hydrolysis.
- Gattermann Koch reaction.

(c) **Preparation of only ketones**
- By treating dialkyl cadmium with acyl chloride
- By treating acid chloride in the presence of anhy. $AlCl_3$
- By treating Grignard reagent with nitrile followed by hydrolysis

- **Physical properties**
  - Lower members of aldehydes and ketones are soluble in water due to the formation of H-bonding and the solubility decreases as the number of carbon increases in the alkyl chain.
  - Their boiling points are higher than the corresponding hydrocarbons and ether but less than the corresponding alcohols due to the absence of hydrogen bonding.
  - Aldehydes can be distinguished from ketones by Tollen's reagent, Fehling solution and Benedict solution.
  - Aldehydes and ketones with α-hydrogen undergo aldol condensation and without, α-hydrogen undergo Cannizzaro's reaction.
  - Reaction with 2,4-DNP can be used to identify the presence of carbonyl group.

- **Carboxylic Acid**
  - Carboxylic acids are the compounds having $-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ functional group. These can be classified as monocarboxylic acid, dicarboxylic acid etc. depending on the number of —COOH group present.

- **Monocarboxylic acids**
  - Carboxylic acids are prepared by
    (a) oxidation of primary alcohols, aldehydes and alkenes
    (b) by hydrolysis of nitriles
    (c) by the treatment of Grignard reagents with carbon dioxide.
    (d) Acidic hydrolysis of esters.

- **Physical properties**
  - Carboxylic acids are polar due to the presence of $-\overset{\overset{\displaystyle O}{\|}}{C}-$ and —OH group. Thus, form H-bonds.
  - They exist in dimeric forms due to intermolecular hydrogen bonding.
  - Acids have high melting points.

- **Acidic nature**
  - Carboxylic acids are most acidic due to the formation of carboxylate ion which is stabilised by resonance.
  - EWG increases the acidity and EDG decreases the acidity of carboxylic acids.
  - More the % *s*-character of α-carbon, more is the acidic character.
  - Peroxy acids are less acidic due to the absence of resonance.
  - Aromatic carboxylic acids are prepared by side chain oxidation of alkyl benzenes.
  - Carboxylic acids are reduced to alcohols with $LiAlH_4$ or H_2 in the presence of copper chromite.
  - — COOH group in benzoic acid is *meta*-directing as well as de-activating in nature.

CHAPTER PRACTICE

OBJECTIVE Type Questions

1 What is the common name of dimethyl ketone?
(a) Ether (b) Acetone
(c) Acetophenone (d) Benzophenone

2 Ethyne + $H_2O \xrightarrow[H_2SO_4]{HgSO_4}$

Product formed in the given reaction is
(a) benzaldehyde (b) acetaldehyde
(c) ethanoic acid (d) ethanoyl chloride

3 The reaction,
$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3\overset{+}{O}} RCHO$
is known as
(a) Etard reaction
(b) Holoform reaction
(c) Gattermann-Koch reaction
(d) Stephen-reaction

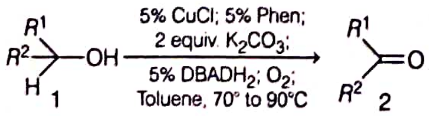
4 Reagent(s) used for the reduction of aldehydes and ketones are
(a) $LiAlH_4$ (b) $NaBH_4$
(c) Catalytic hydrogenation (d) All of these

5 In the vapour phase or in the aprotic solvents carboxylic acids exist as
(a) dimer (b) trimer
(c) tetramer (d) All of these

CASE BASED Questions

Case I

An efficient, aerobic catalytic system for the transformation of alcohols into carbonyl compounds under mild conditions, copper-based catalyst has been discovered. This copper-based catalytic system utilises oxygen or air as the ultimate, stoichiometric oxidants, producing water as the only by-product.



A wide range of primary, secondary, allylic and benzylic alcohols can be smoothly oxidised to the corresponding aldehydes or ketones in good to excellent yields. Air can be conveniently used instead of oxygen without affecting the efficiency of the process. However, the use of air requires slightly longer reaction times.

This process is not only economically viable and applicable to large-scale reactions but it is also environmentally friendly.

The following questions are multiple choice questions. Choose the most appropriate answer : **CBSE SQP 2021**

6 The copper based catalyst mention in the study above can be used to convert
(a) propanol to propanonic acid
(b) propanone to propanoic acid
(c) propanone to propan-2-ol
(d) propan-2-ol to propanone

7 The carbonyl compound formed when ethanol gets oxidised using this copper- based catalyst can also be obtained by ozonolysis of
(a) but-1-ene (b) but-2-ene
(c) ethene (d) pent-1-ene

Or

Which of the following is a secondary allylic alcohol?
(a) But-3-en-2-ol (b) But-2-en-2-ol
(c) Prop-2-enol (d) Butan-2-ol

8 Benzyl alcohol on treatment with this copper-based catalyst gives a compound '*A*' which on reaction with KOH gives compounds '*B*' and '*C*'. Compound '*B*' on oxidation with $KMnO_4$- KOH gives compound '*C*'. Compounds '*A*', '*B*' and '*C*' respectively are
(a) banzaldehyde, benzyl alcohol, potassium salt of benzoic acid
(b) banzaldehyde, potassium salt of benzoic acid, benzyl alcohol
(c) banzaldehyde, benzoic acid, benzyl alcohol
(d) benzoic acid, benzyl alcohol, benzaldehyde

9 An organic compound 'X' with molecular formula C_3H_8O on reaction with this copper based catalyst gives compound 'Y' which reduces Tollen's reagent. 'X' on reaction with sodium metal gives 'Z'. What is the product of reaction of 'Z' with 2-chloro-2-methylpropane?

(a) $CH_3CH_2CH_2OC(CH_3)_3$

(b) $CH_3CH_2OC(CH_3)_3$

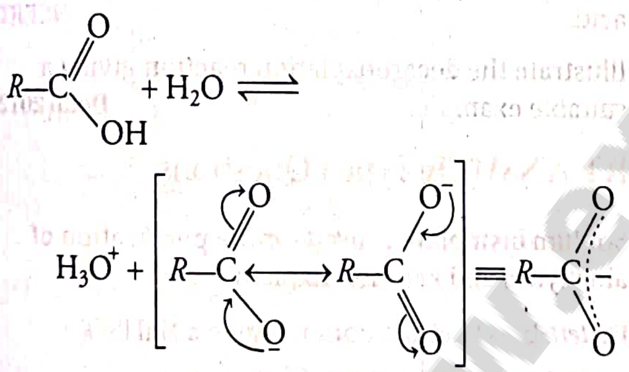
(c) $CH_2=C(CH_3)_2$

(d) $CH_3CH_2CH=C(CH_3)_2$

Case II

Carboxylic acids evolve hydrogen with metals and form salts with alkalies similar to phenols. However, unlike phenols, they react with weaker bases like sodium carbonate and hydrogen carbonate to evolve carbon dioxide.

In aqueous solution, carboxylic acids ionise and exist in dynamic equilibrium between the resonance stabilised carboxylate ions and the hydronium ions.



Resonance stabilisation of carboxylate anion is more than that of undissociated carboxylic acid. Therefore, greater stability of carboxylate ion is responsible for the acidic character of carboxylic acids. Carboxylic acids are more acidic than alcohols because carboxylate anions are more stable than alkoxide ions, so carboxylic acids have strong tendency to release a proton.

In the question that follow Assertion and Reason are given. Reason is purported to the explaination for Assertion. Study carefully and then mark your answers, according to the codes given below.

Marks your answer as :

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

10 **Assertion** Benzoic acid, 3, 4-dinitrobenzoic acid, 4-methoxybenzoic acid are in increasing order of acidic strength.

Reason The have —COOH group.

Or **Assertion** Monochloro ethanoic acid has a higher pK_a than dichloroethanoic acid?

Reason This is because dichloroethanoic acid is a stronger acid than mono chloroethanoic acid.

11 **Assertion** $Cl-CH_2COOH$ is a stronger acid than CH_3COOH.

Reason —Cl group exhibits $+I$ effect.

12 **Assertion** $2R-COOH + 2Na \longrightarrow 2R-COONa + H_2\uparrow$

Reason Reaction shows the acidic nature of carboxylic acid.

13 **Assertion** Acid chloride is formed when carboxylic acids are treated with thionyl chloride.

Reason When carboxylic acid are treated with thionyl chloride, acid chloride is formed. The reaction is as follows :

$$\underset{\text{Acetic acid}}{CH_3COOH} + SOCl_2 \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + SO_2\uparrow + HCl\uparrow$$

ASSERTION and REASON

■ **Directions** (Q. Nos. 14-21) *In the following questions. an Assertion (A) is followed by a corresponding Reason (R) Use the following keys to choose the appropriate answer.*

(a) Both (A) and (R) are correct, (R) is the correct explanation of (A).

(b) Both (A) and (R) are correct, (R) is not the correct explanation of (A).

(c) (A) is correct; (R) is incorrect.

(d) (A) is incorrect; (R) is correct.

14 **Assertion (A)** α-hydrogen atoms of carbonyl compounds are acidic.

Reason (R) The strong electron releasing effect of the carbonyl group make the stabilisation of the conjugate base by the resonance.

15 **Assertion** (A) IUPAC name of $HOOC\text{-}(CH_2)_2\text{-}COOH$ is butane-dioic acid.

Reason (R) In compounds containing more than one carboxyl group, '-e' of the alkane is retained, and prefix 'di' is added to the term-'oic'.

16 **Assertion** (A) Carboxylic acids are more acidic than phenols.

Reason (R) Phenols are *ortho* and *para*-directing.

17 **Assertion** (A) Carboxylic acids have higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses.

Reason (R) More extensive association of carboxylic acid molecules through intermolecular hydrogen bonding is responsible for the high boiling point of carboxylic acid.

18 **Assertion** (A) Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

Reason (R) Aromatic aldehydes are almost as reactive as formaldehyde.

19 **Assertion** (A) Aldehydes and ketones, both react with Tollen's reagent to form silver mirror.

Reason (R) Both aldehydes and ketones contain a carbonyl group.

20 **Assertion** (A) Formaldehyde is a planar molecule.

Reason (R) It contains sp^2-hybridised carbon atom.

21 **Assertion** (A) Compounds containing —CHO group are easily oxidised to corresponding carboxylic acids.

Reason (R) Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.

VERY SHORT ANSWER Type Questions

22 Why there is a large difference in the boiling points of butanal and butan-1-ol?

23 Dipole moment of CH_3CH_2CHO (propanal) (2.5 D) is greater than that of but-1-ene (0.30 D). Why?

24 Explain cyclohexanone is more reactive with HCN than cyclopentanone.

25 Oxidation of ketones involve carbon-carbon bond cleavage. Name the products formed on the oxidation of 2,5-dimethyl hexan-3-one.

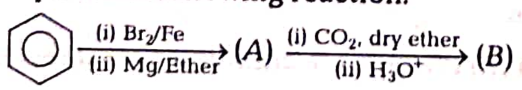
26 Name any two reagents which are used to distinguish between aldehydes and ketones.

27 How will you convert bromobenzene to 1-phenyl ethanol?

28 pK_a of chloroacetic acid is lower than pK_a of acetic acid. Why?

29 Why is C—O bond shorter in RCOOH than in RCHO?

30 Complete the following reaction.

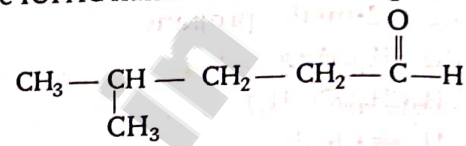


31 Consider the following reaction,

$$2R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[P_2O_5,\Delta]{H^+,\Delta} \text{Product } A$$

Identify the product A.

32 Write the IUPAC name of the following compound.



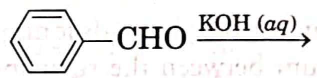
33 Draw the structures of vanillin, cinnamaldehyde and salicylaldehyde.

34 What is Clemmensen reduction? **All India 2013**

Or Illustrate the following name reaction giving suitable example: Clemmensen reduction

Delhi 2012, 2009, 2008, All India 2011, 2010

35 Complete the reaction,



36 Draw the structural formula of hex-2-en-4-ynoic acid. **NCERT**

37 Illustrate the decarboxylation reaction giving a suitable example. **Delhi 2012**

SHORT ANSWER Type I Questions

38 Sodium bisulphite is used for the purification of aldehydes and ketones. Explain.

39 Di-*tert*-butyl ketone does not give a $NaHSO_3$ adduct but acetone does. Give reason.

40 Why is it necessary to control the pH during the reaction of aldehydes and ketones with ammonia derivatives?

41 Write the products of oxidation of

(i) pentan-2-one and (ii) pentan-3-one.

Are the major products same or different? Explain.

42 Convert

(i) benzonitrile to acetophenone

(ii) 1, 2-dicyclohexylethene to cyclohexanone?

43 Complete the following reaction and explain the formation of products.

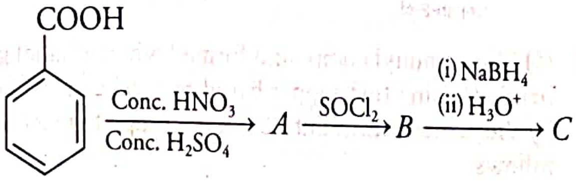
(i) $HCOOH \xrightarrow{\text{Conc. } H_2SO_4}$

(ii) $CH_3COOH + CH_3OH \xrightarrow{\text{Conc. } H_2SO_4}$

44 Why benzoic acid does not undergo Friedel-Crafts reaction?

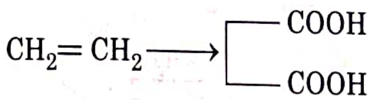
45 An aldehyde $A(C_{11}H_8O)$, which does not undergo self aldol condensation, gives benzaldehyde and 2 moles of B on ozonolysis. Compound B on oxidation with silver ion gives oxalic acid. Identify the compounds A and B.

46 Identify the missing compounds in the following reaction sequence :

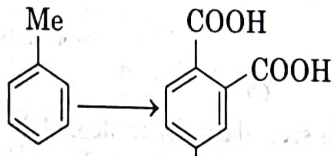


47 Convert
(i) Acetaldehyde to formaldehyde
(ii) Propanal to butanone

48 How will you bring about the following conversions?

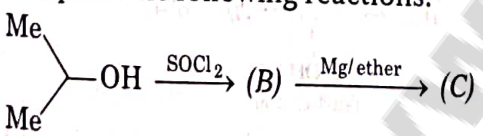
(i) 

(Succinic acid)

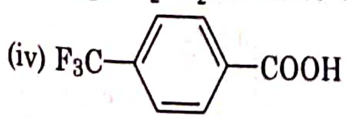
(ii) 

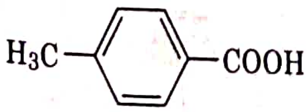
(Toluene) (Benzene-1,2,4-tricarboxylic acid)

49 Complete the following reactions:



50 Describe the following.
(i) Cannizzaro reaction
(ii) Cross aldol condensation NCERT

51 Which acid of each pair shown here would you expect to be stronger?
(i) CH_3COOH or CH_2FCOOH
(ii) CH_2FCOOH or $CH_2ClCOOH$
(iii) $CH_2FCH_2CH_2COOH$ or CH_3CHFCH_2COOH
(iv) 

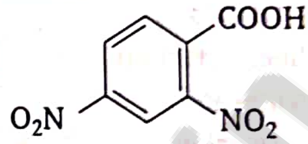
Or 

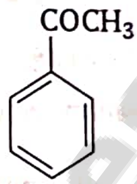
All India 2013; NCERT Intext

SHORT ANSWER Type II Questions

52 (i) Give the structures of the following:
(a) Phthaldehyde
(b) 3-methyl cyclohexane carbaldehyde
(c) 3-methylbut-2-enoic acid

(ii) Write the IUPAC names of the following structures:

(a) 

(b) 

(c) 

53 Give names of the reagents to bring about the following transformations:
(i) Benzoyl chloride to benzaldehyde
(ii) Benzene to benzaldehyde
(iii) Benzene to acetophenone

54 Complete the following equations, giving the names of the reactants and the products.

(i) $C_6H_6 + \ldots \xrightarrow{\text{Anhy. AlCl}_3} C_6H_5COCH_3$

(ii) $(CH_3)_2CO \xrightarrow{\text{LiAlH}_4}$

55 What is α-hydrogen in a carbonyl compounds? Write the similarities and differences on the reactivity of the compounds CH_3CHO and C_6H_5CHO with the reagents:
(i) NaOH (ii) Tollen's reagent

56 Acetone on reaction with HCN gives one compound, whereas acetaldehyde gives two compounds that are difficult to separate. Explain why?

57 Show how each of the following compounds can be converted to benzoic acid?
(i) Benzamide (ii) Propyl benzene

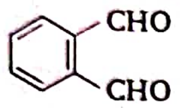
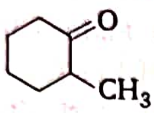
58 Account for the following differences in the acidic character of the following.
(i) $Me_3C-CH_2-COOH > Me_3SiCH_2COOH$
(ii) $H_2C=CHCH_2COOH > CH_3CH_2COOH$
(iii) $N \equiv C-CH_2COOH > CH_3COCH_2-COOH$

59 Identify the products A and B in the following reactions:

(i) $CH_3COOH \xrightarrow{Cl_2/P} (A) \xrightarrow{aq.\ NaOH} (B)$

(ii) $CH_3COOH \xrightarrow{NH_4OH} (A) \xrightarrow{\text{Heat}} (B)$

60 Write down the IUPAC and common name for the following.

(i)  (ii) 

(iii) $CH_2=CHCHO$

61 Write the chemical equations to illustrate the following name reactions.

(i) Wolff-Kishner reduction

(ii) Aldol condensation

(iii) Cannizzaro reaction **Delhi 2014**

LONG ANSWER Type Questions

62 (i) Write the chemical equations when acetic acid reacts with

(a) Br_2 in the presence of phosphorus.

(b) Cl_2 in the presence of phosphorus.

(ii) Give two reactions in which aliphatic aldehydes differ from aromatic aldehydes?

63 (i) Convert

(a) Benzoic acid to benzaldehyde

(b) Propanone to propane

(ii) Arrange the following compounds in the decreasing order of their acidic strength.

CH_3CH_2COOH, $CH_3CH_2CH(F)COOH$, $CH_3CH(F)CH_2COOH$, $(CH_3)_2CHCOOH$

64 What is meant by the following terms? Give an example of the reaction in each case.

(i) Hemiacetal (ii) Oxime

(iii) Ketal (iv) Imine

(v) Schiff's base

65 Differentiate between the following:

(i) Propanoic acid and acrylic acid ($CH_2=CH—COOH$)

(ii) 2-bromopropanoic acid ($CH_3CHBrCOOH$) and pyruvic acid ($CH_3COCOOH$).

(iii) Malonic acid $\begin{pmatrix} COOH \\ | \\ CH_2 \\ | \\ COOH \end{pmatrix}$ and succinic acid $\begin{pmatrix} CH_2COOH \\ | \\ CH_2COOH \end{pmatrix}$.

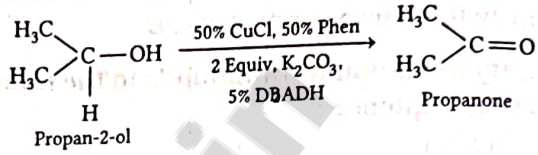
66 Write any three mild oxidising agents that are used to distinguish aldehydes from ketones and explain the reactions involved.

ANSWERS

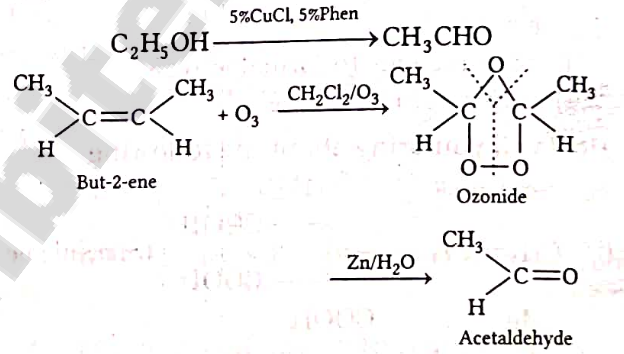
1 (*b*) **2** (*b*) **3** (*d*) **4** (*d*) **5** (*a*)

6 (*d*) The copper based catalyst mention in the study can be used to convert propan-2-ol to propanone.

Reaction is as follows:

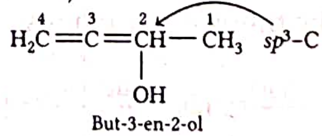


7 (*b*) The carbonyl compound formed when ethanol gets oxidised using this copper based catalyst can be obtained by the ozonolysis of but - 2 - ene. Complete reaction is as follows :

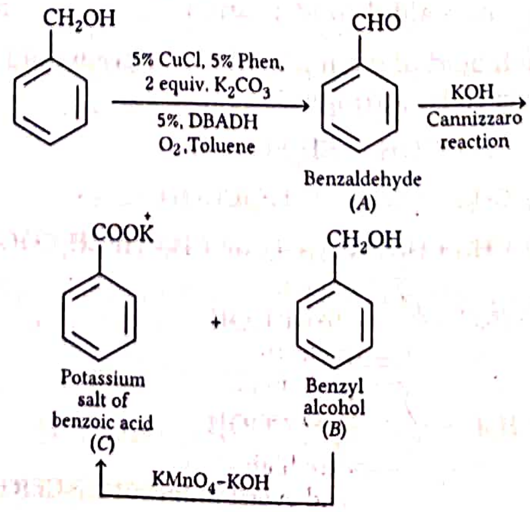


Or

(*a*) But-3-en-2-ol is a secondary allylic alcohol. In these alcohols, the —OH group is attached to a sp^3-hybridised allylic carbon (carbon atom next to the C—C double bond).



8 (*b*) Compounds *A*, *B* and *C* respectively are benzaldehyde, potassium salt of benzoic acid, benzyl alcohol. Complete reaction is as follows:



9 (*c*) The product of reaction of '*Z*' with 2-chloro - 2-methylpropane is $CH_2 = C(CH_3)_2$. Complete reactions are as follows:

$$\underset{\text{Propanol (X)}}{CH_3CH_2CH_2OH} \xrightarrow[\text{2 equiv. } K_2CO_3]{5\%\ CuCl,\ 5\%\ Phen,} \underset{\text{Propanal (Y)}}{CH_3CH_2CHO}$$

$$\downarrow \text{Na-metal}$$

$$\underset{\text{Sodium propoxide}}{CH_3CH_2CH_2\bar{O}Na} + \underset{\text{2-chloro-2-methylpropane}}{(CH_3)_3{-}C{-}Cl} \xrightarrow[\text{reaction}]{\text{Elimination}} \underset{\text{2-methyl prop-1-ene}}{CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2} + NaOH + CH_3(CH_2)_2OH$$

10 (*c*) 4-methoxybenzoic acid < benzoic acid < 3, 4-dinitro benzoic acid. Only (A) is correct.

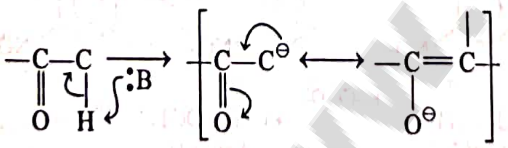
Or (*a*) Both (A) and (R) are true and (R) is correct explanation of (A).

11 (*c*) $Cl-CH_2COOH$ is a stronger acid than CH_3COOH. It is because — Cl group exhibits $-I$ effect which makes the carboxylate ion more stable. Higher the stability of carbohydrates ion, easier is the removal of proton from the carboxylic acid and stronger is the acid. In CH_3COOH, — CH_3 group has $+I$ effect which destabilised it. Hence, CH_3COOH is a weaker acid. Only (A) is correct.

12 (*b*) Both (A) and (R) are true but (R) is not correct explanation of (A).

13 (*a*) Both (A) and (R) are correct and (R) is correct explanation of (R).

14 (*c*) The acidity of α-hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.



Hence, (A) is correct but (R) is incorrect.

15 (*a*) IUPAC name of $HOOC \leftarrow CH_2 \rightarrow_2 COOH$ is butane-dioic acid. For compounds containing more than one carboxyl group, the ending '-e' of the alkane is retained. The number of carboxyl groups are indicated by adding the multiplicative prefix, di, tri etc., to the term 'oic'. Thus both A and R is correct and R is the correct explanation of A.

16 (*b*) Carboxylic acids are stronger acids than phenols because carboxylate ion is much more resonance stabilised than phenoxide ion as negative charge is delocalised over two electronegative O^- atom in carboxylate anion while in phenol, negative charge is localised at only one O^--atom.

17 (*a*) Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. Hence, both (A) and (R) are correct and (R) is the correct explanation of (A).

18 (*c*) Aromatic aldehydes are less reactive than aliphatic aldehyde like formaldehyde. Cannizzaro's reaction is shown by aldehydes which do not contain any α-H atom. Such aldehydes in the presence of concentrated solution of an alkali undergo self oxidation-reduction to give a mixture of alcohol and a salt of the carboxylic acid. For example, formaldehyde (HCHO) gives methanol and sodium methanoate.

$$\underset{\text{(2 molecules of formaldehyde methanal)}}{H-\overset{H}{\overset{|}{C}}=O + H-\overset{H}{\overset{|}{C}}=O} \xrightarrow{\text{NaOH (conc.)}} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Sodium methanoate}}{H-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{Na}}$$

Hence, (A) is correct but (R) is incorrect.

19 (*d*) Ketones do not react with Tollen's reagent to give silver mirror test, because ketone cannot reduce silver ions of Tollens's reagent to give silver metal.

Aldehydes react with Tollen's reagent to form silver mirror. Hence, (A) is incorrect but (R) is correct.

20 (*a*) The carbon-oxygen bond is carbonyl group ($\rangle C = O$) is composed of one sigma (σ) and one pi (π) bond. The carbon in carbonyl group is sp^2**-hybridised**. Therefore, the three bonds in the carbonyl carbon are **planar** and trigonal with bond angle of 120°. (A) and (R) both are correct and (R) is the correct explanation of (A).

21 (*b*) (A) and (R) both are correct statement but (R) is not correct explanation of (A).

Easy oxidation of aldehydes is due to the presence of a hydrogen atom on the carbonyl group.

$$R-\overset{H}{\overset{|}{C}}=O \xrightarrow{[O]} R-C\begin{matrix}\nearrow O \\ \searrow OH\end{matrix}$$

Carboxylic acids can be reduced to alcohol by using reducing agents such as $LiAlH_4$ or better by diborane.

$$RCOOH \xrightarrow{LiAlH_4} RCH_2OH + H_2O$$

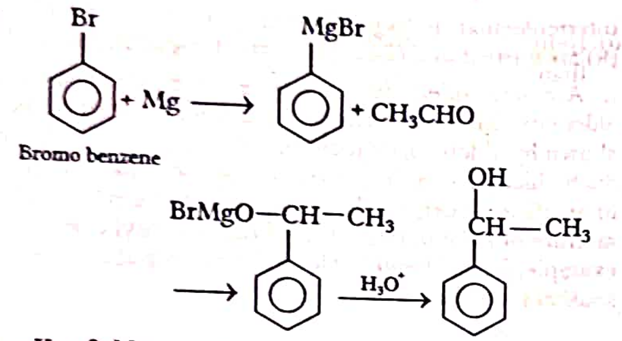
22 Boiling point of butanal is lower that butan-1-ol due to the absence of intermolecular hydrogen bonding.

23 **Hint** Due to the presence of (polar group) in propanal.

24 **Hint** Cyclohexanone act as better electrophile.

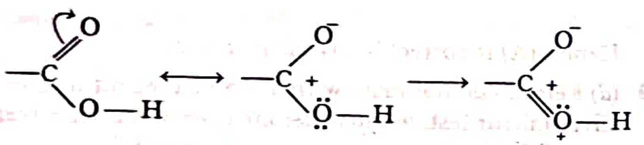
25 **Hint** $CH_3-\underset{CH_3}{\underset{|}{CH}}-COOH,\ CH_3-\overset{CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}-CH_2COOH,$

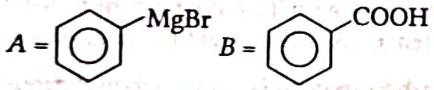
26 **Hint** Tollen's reagent and Fehling's reagent.

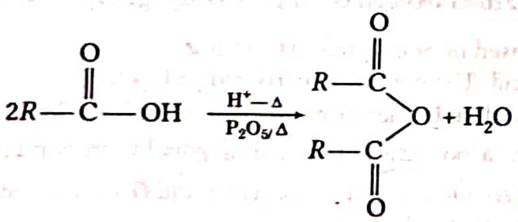
27 

28 pK_a of chloroacetic acid is lower that pK_a of acetic acid because acility of carboxylic acids increases due to the presence of electron withdrawing groups.

29 The C— O bond is shorter in RCOOH than in RCHO due to the following possible resonance structures :

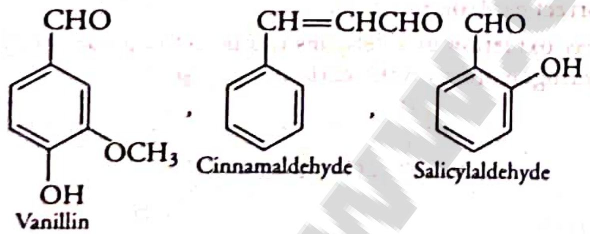


30 Hint 

31 

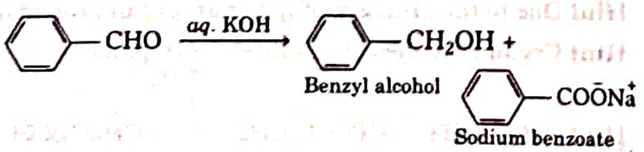
Acid anhydride

32 4-methylpentan-1-al

33 

34 Clemmenson reduction involves the reduction of carbonyl group $\rangle C=O$ to $\rangle CH_2$ group and it is carried out in the presence of in amalgam and conc. HCl.

$$\rangle C=O + 4[H] \xrightarrow{\text{Zn-Hg/Conc. HCl}} \underset{\text{Hydrocarbon}}{\rangle CH_2} + H_2O$$

35 

36 $\overset{6}{CH_3}-\overset{5}{C}\equiv\overset{4}{C}-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{\underset{}{C}}(=O)-OH$

37 The loss of CO_2 molecule from a carboxylic acid to form hydro carbons is called decarboxylation.

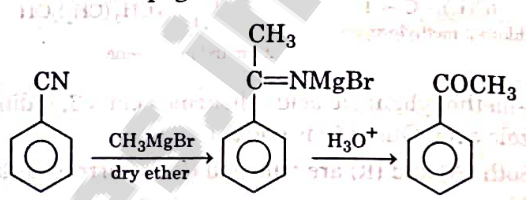
Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3 : 1).

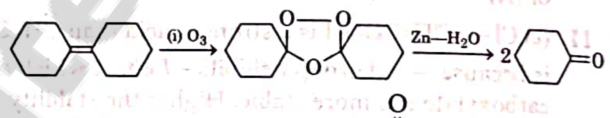
38 Refer to text on page 315.

39 Hint Due to steric hinderance caused by the bulky *tert*-butyl groups, the bisulphite ion cannot easily approach the carbonyl group for addition.

40 Hint NH_3 is a base. In acidic medium, it can form anilinium ion.

41 Refer to text on page 318.

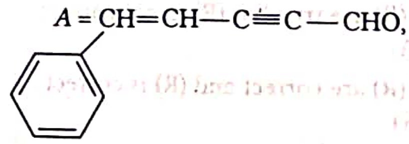
42 (i) 

(ii) 

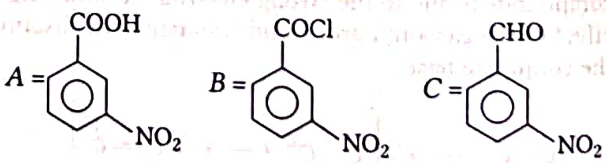
43 (i) $CO + H_2SO_4 + H_2O$ (ii) $CH_3O-\overset{O}{\overset{\|}{C}}CH_3$

44 Refer to text on page 342.

45 Hint Aldehyde A is



B is OHC — COOH

46 

47 (i) $\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{K_2Cr_2O_7} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH}$

$\underset{\text{Sodium acetate}}{CH_3CO\overset{-}{O}\overset{+}{Na}} \xrightarrow{\text{Sodalime}} \underset{\text{Methane}}{CH_4} \xrightarrow{Cl_2} \underset{\text{Methyl chloride}}{CH_3Cl}$

$\downarrow AgOH$

$\underset{\text{Formaldehyde}}{HCHO} \xleftarrow{Cu} \underset{\text{Methanol}}{CH_3OH}$

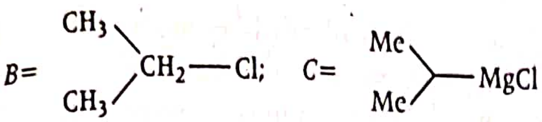
(ii) $CH_3CH_2CHO + CH_3MgBr \xrightarrow{H_2O}$

$CH_3CH_2CH(OH)CH_3 \xrightarrow{CrO_3} CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_3$

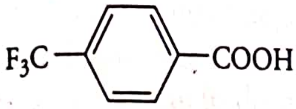
48 (i) $CH_2=CH_2 \xrightarrow{Br_2} Br\,CH_2\,CH_2\,Br \xrightarrow{CN^-}$

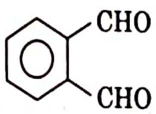
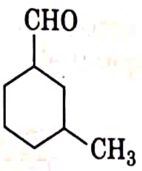
$NC\,CH_2\,CH_2\,CN \xrightarrow{H_3O^+} \begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array}$

(ii) **Hint** Alkylation followed by oxidation.

49 

50 (i) **Cannizzaro reaction** Refer to text on page 321.
(ii) **Cross aldol condensation** Refer to text on page 321.

51 (i) CH_2FCOOH is a stronger acid.
(ii) CH_2FCOOH is a stronger acid.
(iii) CH_3CHFCH_2COOH is a stronger acid.
(iv)  is a stronger acid.

52 Hint
(i) (a)  (b) 
(c) $CH_3-\overset{CH_3}{\overset{|}{C}}=CH-COOH$
(ii) (a) 2, 4-dinitrobenzoic acid (b) Acetophenone
(c) 4-methyltoluene.

53 (i) Refer to text on page 312.
(ii) Refer to text on page 313.
(iii) Refer to text on page 313.

54 (i) CH_3COCl
(ii) $CH_3-\overset{OH}{\overset{|}{CH}}-CH_3$

55 (i) CH_3CHO will give aldol condensation with NaOH while C_6H_5CHO does not.
(ii) CH_3 CHO gives positive test with Tollen's reagent whereas C_6H_5CHO does not.

56 Refer to text on page 315.

57 (i) Refer to text on page 337 (ii) Refer to text on page 337.

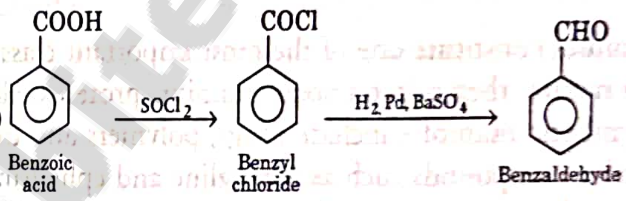
58 Hint
(i) Carbon is more electronegative than silicon.
(ii) sp^2-hybridised carbon is more electronegative than sp^3-hybridised carbon.
(iii) sp-hybridised carbon of $C \equiv N$ is more electronegative than sp^2 hybridised carbon of $C = O$.

59 (i) $A = ClCH_2COOH$, $B = HO-CH_2-COOH$
(ii) $A = CH_3COO^-NH_4^+$ $B = CH_3CONH_2$

60 Refer to text on pages 308 and 309.

61 (i) Refer to text on page 319. (ii) refer to text on page 320.
(iii) Refer to text on pages 321.

62 (i) **Hint**
(a) $Br-CH_2COOH$ (b) $Cl-CH_2COOH$
(ii) **Hints** (a) Aliphatic aldehydes being more reactive reduce Fehling's solution to red ppt. of Cu_2O while aromatic aldehydes do not.
(b) Aromatic aldehydes on treatment with an alcoholic solution of KCN undergo benzoin condensation but aliphatic aldehydes do not.

63 (i) 
(ii) Refer to text on page 340.

64 (i) Refer to text on page 316.
(ii) Refer to text on page 317.
(iii) Refer to text on page 316.
(iv) Refer to text on page 317.
(v) **Schiff's base** When an aldehyde or ketone reacts with primary aliphatic or aromatic amines, the compound formed is called Schiff's base or azomethine.

$$\underset{\text{Aldehyde}}{R-CH=O}+\underset{\text{Primary amine}}{H_2N-R'}\xrightarrow{H^+}\underset{\text{Schiff's base}}{R-CH=N-R'}+H_2O$$

65 (i) **Hint** Acrylic acid is stronger than propanoic acid (acidity depends upon stability of its conjugate base).
(ii) **Hint** EWG increases the acidity of carboxylic acids.
(iii) **Hint** pK_a value of succinic acid is higher than pK_a value of malonic acid.

66 Refer to text on page 318 and 319.

09

AMINES

Amines constitute one of the most important class of organic compounds. In nature, they occur among vitamins, proteins, alkaloids and hormones. Synthetic examples include drugs, polymers and dyestuffs. Biologically active compounds such as adrenaline and ephedrine, both containing secondary amino group are used to increase the blood pressure. Novocain, a synthetic amino compound is used as an anaesthetic in dentistry whereas benadryl is anantihistaminic drug containing tertiary amino group. Quaternary ammonium salts are used as surfactants.

Diazonium salts are intermediates used in the preparation of a variety of aromatic compounds.

CHAPTER CHECKLIST

- Structure, Classification Nomenclature and Preparation of Amines
- Properties of Amines
- Diazonium Salts

|TOPIC 1|
Structure, Classification, Nomenclature and Preparation of Amines

Amines are the derivatives of ammonia, obtained by the replacement of one, two or three hydrogen atoms by alkyl/aryl groups. e.g.

$$\underset{1^\circ\text{ amine}}{CH_3—NH_2}, \quad \underset{2^\circ\text{ amine}}{CH_3—NH—CH_3}, \quad \underset{3^\circ\text{ amine}}{CH_3—N\begin{matrix} CH_3 \\ CH_3 \end{matrix}}$$

STRUCTURE OF AMINES

Structure of amines is described below:

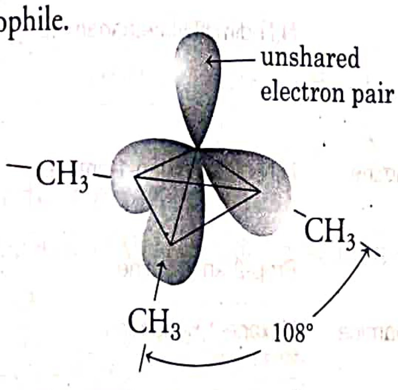
(i) Like ammonia, nitrogen atom of amines is trivalent and carries an unshared pair of electrons. Therefore, the N orbitals in amines are sp^3-hybridised and the geometry of amines is pyramidal.

(ii) The ground state electronic configuration of N is $1s^2, 2s^2, 2p_x^1 2p_y^1 2p_z^1$. Here, one 2$s$-orbital and three 2$p$-orbitals are hybridised to form four sp^3-hybridised orbitals, three of them have one electron and the fourth orbital has one lone pair of electrons.

(iii) Each of the three sp^3-hybridised orbitals of nitrogen overlap with orbitals of carbon or hydrogen depending upon the composition of the amines. The fourth orbital of N contains an unshared pair of electrons, in all amines.

(iv) Due to the presence of unshared pair of electrons, the angle C—N—E (where E is C or H) is less than 109.5°.
e.g. In trimethylamine, angle is 108°.

(v) Due to the presence of lone pair of electrons on nitrogen which can be donated, amines act as a nucleophile.



Pyramidal shape of trimethylamine

CLASSIFICATION OF AMINES

Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms in ammonia molecule replaced by alkyl (R) or aryl (Ar) groups. Thus, we can show the sequence of classification of amine from ammonia.

$$\underset{\text{Ammonia}}{NH_3} \xrightarrow[+R]{-H} \underset{\text{Primary (1°)}}{R—NH_2} \xrightarrow[+R']{-H} \underset{\text{Secondary (2°)}}{R—NH—R'} \xrightarrow[+R'']{-H} \underset{\text{Tertiary (3°)}}{R—N(R')(R'')}$$

Degree and functional group of various amines

S. No.	Amine	n (no. of H-atoms attached to N)	Type of amine	Functional group
1.	$R—N(H)—H$	2	1° (primary)	$—NH_2$
2.	R_2NH	1	2° (secondary)	—NH—
3.	R_3N	0	3° (tertiary)	$\gt N—$

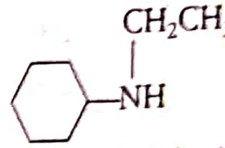
Simple amines When all the alkyl/aryl groups are same, the amines are said to be simple amines e.g.

$$\underset{2°\text{ amine}}{(CH_3)_2NH}, \quad \underset{3°\text{ amine}}{(CH_3CH_2)_3N}$$

Mixed amines When all the alkyl/aryl groups are different, the amines are said to be mixed amines.

e.g.

$$\underset{\substack{\text{Ethylmethyl amine}\\(2°)}}{CH_3—NH—CH_2CH_3},$$



Cyclohexyl ethyl amine
(2°)

NOMENCLATURE OF AMINES

Rules and steps to be followed while naming of the amines are given below:

(i) In common system, an aliphatic amine is named by adding suffix 'amine' to the name of the alkyl group attached to the nitrogen atom, e.g. methylamine.

(ii) In 2° and 3° amines, when two or more groups are the same, the prefix di or tri is used before the name of the alkyl group.

e.g. $$\underset{\text{Trimethylamine}}{CH_3—N(CH_3)—CH_3}$$

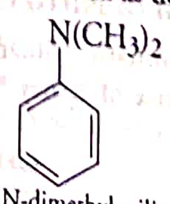
(iii) In IUPAC system, amines are named as alkanamines, derived by the replacement of 'e' of alkane by word 'amine'.

e.g. $$\underset{\text{Methanamine}}{CH_3NH_2}, \quad \underset{\text{N, N-dimethylmethanamine}}{CH_3—N(CH_3)—CH_3}$$

(iv) If more than one amino group is present at different positions in the parent chain, then by assigning number, their positions are specified to the carbon atoms bearing $—NH_2$ groups and the terminal 'e' of the name of the parent hydrocarbon is retained.

e.g. $$\underset{\text{Ethane-1,2-diamine}}{H_2N—CH_2—CH_2—NH_2}$$

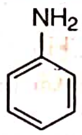
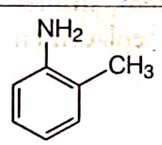
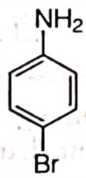
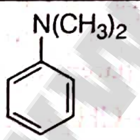
(v) The simplest arylamine/aromatic amine in which the $—NH_2$ group is directly attached to the benzene ring, i.e. $C_6H_5NH_2$ is called **aniline** and the substituted aromatic amines are named as derivatives of aniline.



N, N-dimethylaniline

(vi) In IUPAC system, the terminal 'e' of arene is replaced by 'amine'. e.g. $C_6H_5—NH_2$ (Benzenamine)

Nomenclature of some important alkanamines and arylamines

Amine	Common name	IUPAC name
$CH_3-CH_2-NH_2$	Ethylamine	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	*n*-propylamine	Propan-1-amine
$CH_3-\underset{\underset{NH_2}{\vert}}{CH}-CH_3$	Isopropylamine	Propan-2-amine
$CH_3-\underset{\underset{H}{\vert}}{N}-CH_2-CH_3$	Ethylmethylamine	N-methylethanamine
$CH_3-\underset{\underset{CH_3}{\vert}}{N}-CH_3$	Trimethylamine	N,N-dimethylmethanamine
$C_2H_5-\underset{\underset{C_2H_5}{\vert}}{N}-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$	N,N-diethylbutylamine	N,N-diethylbutan-1-amine
$NH_2-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H_2$	Allylamine	Prop-2-en-1-amine
$NH_2-(CH_2)_6-NH_2$	Hexamethylenediamine	Hexane-1,6-diamine
	Aniline	Aniline or Benzenamine
	*o*-toluidine	2-aminotoluene
	*p*-bromoaniline	4-bromobenzenamine or 4-bromoaniline
	N,N-dimethylaniline	N,N-dimethylbenzenamine

PREPARATION OF AMINES

Amines are prepared by the following methods:

By the Reduction of Nitro Compounds

Both aliphatic and aromatic primary amines can be prepared by the reduction of nitro compounds either catalytically with H_2 in the presence of Raney Ni, Pt or Pd or chemically with active metal in acidic medium.

e.g.

$$\underset{\text{Nitromethane}}{CH_3NO_2} + 3H_2 \xrightarrow[\text{Ethanol}]{\text{Raney Ni/Pt}} \underset{\text{Methylamine}}{CH_3NH_2} + 2H_2O$$

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 3H_2 \xrightarrow[\text{or Fe + HCl}]{\text{Sn + HCl}} \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$

Reduction with Fe scrap and HCl is preferred because $FeCl_2$ formed gets hydrolysed to release HCl during the reaction. Therefore, only a small amount of HCl is needed to initiate the reaction.

By the Reduction of Nitriles

Reduction of nitriles with lithium aluminium hydride ($LiAlH_4$) or catalytic hydrogenation produces primary amines. This method is used to prepare amines containing one carbon atom more than the starting amine.

$$R—C\equiv N \xrightarrow[LiAlH_4 \text{ or } Na(Hg) / C_2H_5OH]{\text{Raney Ni}/H_2} R—CH_2—NH_2$$

By the Reduction of Amides

On reduction with $LiAlH_4$, amides yield amines.

e.g. $$R—\overset{\overset{\large O}{\|}}{C}—NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4\text{, ether}} R—CH_2—NH_2$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4\text{, ether}} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

By Hofmann Bromamide Degradation Reaction

This reaction is used for preparing amine containing one carbon less than the starting amide. This method was developed for the preparation of primary amines by reacting an amide with Br_2 / Cl_2 in an aqueous or ethanolic solution of NaOH/KOH.

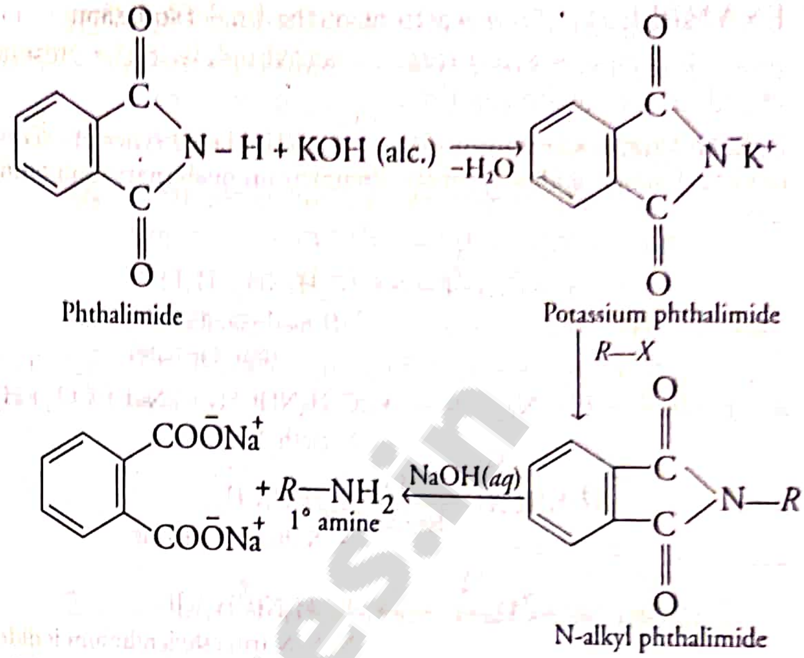
In this reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the N-atom.

$$R—\overset{\overset{\large O}{\|}}{C}—NH_2 + Br_2 + 4NaOH \longrightarrow R—NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

e.g. $$\underset{\text{Amide}}{CH_3CH_2\,CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Amine}}{CH_3CH_2NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

Gabriel Phthalimide Synthesis

When a phthalimide is treated with ethanolic KOH, it forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines.



This method produces only primary amines without the traces of secondary or tertiary amines. So, this method is preferred for the synthesis of primary amines.

Note This method is not useful for the preparation of aromatic primary amines because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

Ammonolysis of Alkyl Halides

This reaction is a nucleophilic substitution reaction in which ammonia acting as a nucleophile, displaces the halogen atom. This process of cleavage of C—X bond by ammonia is called ammonolysis. Alkyl or benzyl or aryl halides on reaction with ethanolic solution of ammonia undergoes nucleophilic substitution reaction because in these halides, carbon-halogen bond is easily cleaved by a nucleophile.

$$\underset{\text{Ammonia}}{:NH_3} + \underset{\text{Alkyl halide}}{R—X} \xrightarrow[\text{Sealed tube}]{373\text{ K}} \underset{\substack{\text{Substituted}\\\text{ammonium salt}}}{R—\overset{+}{N}H_3X^-} \underset{}{\overset{NH_3}{\rightleftharpoons}} \underset{1^\circ\text{amine}}{RNH_2}$$

$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\substack{\text{Quaternary}\\\text{ammonium salt}}}{R_4\overset{+}{N}\overset{-}{X}}$$

This primary amine behaves as a nucleophile and on subsequent reaction with alkyl halide forms 2°, 3° amines and finally forms quaternary ammonium salt. This method cannot be used for the preparation of arylamine (unless benzene ring is activated by EWG at *o*- and *p*-positions). The free amine can be obtained from the ammonium salt by the treatment with a strong base.

$$R—\overset{+}{N}H_3\,\overset{-}{X} + NaOH \longrightarrow R—NH_2 + H_2O + Na^+X^-$$

Order of reactivity of halides with NH_3 is :

$$R—I > R—Br > R—Cl > R—F$$

EXAMPLE |1| Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

Sol. **Hofmann's ammonolysis reaction** In the presence of excess of methyl iodide, aniline (primary amine) forms quaternary ammonium salt.

$$\underset{\text{Aniline}}{C_6H_5\ddot{N}H_2} + CH_3{-}I \longrightarrow \underset{\substack{\text{N-methylanilinium iodide}\\ \text{(Intermediate)}}}{[C_6H_5\overset{+}{N}H_2CH_3]\,I^-}$$

$$2[C_6H_5\overset{+}{N}H_2CH_3]\,\bar{I} + Na_2CO_3 \longrightarrow \underset{\text{N-methylaniline}}{2C_6H_5NHCH_3} + 2NaI + CO_2 + H_2O$$

$$C_6H_5\ddot{N}HCH_3 \xrightarrow[Na_2CO_3]{CH_3I} \underset{\text{N, N-dimethylaniline}}{C_6H_5N(CH_3)_2}$$

$$C_6H_5\ddot{N}(CH_3)_2 + CH_3{-}I \longrightarrow \underset{\text{N, N, N-trimethylanilinium iodide}}{[C_6H_5\overset{+}{N}(CH_3)_3]I^-}$$

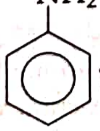
$$2[C_6H_5\overset{+}{N}(CH_3)_3]\,\bar{I} + Na_2CO_3 \longrightarrow \underset{\substack{\text{N, N, N-trimethyl}\\ \text{anilinium carbonate}}}{[C_6H_5\overset{+}{N}(CH_3)_3]_2\,CO_3^{2-}} + 2NaI$$

TOPIC PRACTICE 1

OBJECTIVE Type Questions

1. Which of the following is a 3° amine? **NCERT Exemplar**
   (a) 1-methylcyclohexylamine
   (b) Triethylamine
   (c) *tert*-butylamine
   (d) N-methylaniline

2. IUPAC name of $H_2N-CH_2-CH_2-NH_2$ is
   (a) ethane-1, 3-diamine
   (b) ethane-1, 2-diamine
   (c) ethyn-1, 2, diamine
   (d) ethen-1, 2, diamine

3. What is the common name of 

?
   (a) Aniline (b) Benzenamine
   (c) Toluidine (d) None of these

4. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine? **NCERT Exemplar**
   (a) H_2(excess)/Pt (b) $LiAlH_4$ in ether
   (c) Fe and HCl (d) Sn and HCl

5. Which of the following products is formed in the given reaction?
$$R-CONH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4}$$
   (a) RNH_2 (b) RCH_2NH_2
   (c) $RCH_2CH_2NH_2$ (d) RCN

6. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is .... **NCERT Exemplar**
   (a) excess H_2
   (b) Br_2 in aqueous NaOH
   (c) iodine in the presence of red phosphorus
   (d) $LiAlH_4$ in ether

7. Propanamide on reaction with bromine in aqueous NaOH gives **CBSE SQP 2021**
   (a) propanamine
   (b) ethanamine
   (c) N-methylethanamine
   (d) propanenitrile

8. IUPAC name of product formed by reaction of methyl amine with two moles of ethyl chloride **CBSE SQP 2021**
   (a) N,N-dimethylethanamine
   (b) N,N-diethylmethanamine
   (c) N-methylethanamine
   (d) N-ethyl ,N-methylethanamine

VERY SHORT ANSWER Type Questions

9. Give the name of any two naturally occurring amines.

10. Draw the structure of N-methylethanamine. **All India 2013**

11. Draw the structure of 2-aminotoluene.

12. Write the IUPAC name of the following compound and classify it into primary, secondary and tertiary amine.
$$m\text{-}BrC_6H_4NH_2$$

13. Write the IUPAC name of the following compound.
$$CH_3-\underset{\substack{|\\ NH_2}}{CH}-CH_2-CHO$$
All India 2014, 13

14. Write the IUPAC name of the following compound:
$$(CH_3)_2N-CH_2CH_3$$
Delhi 2017

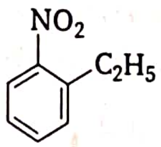
15. Write the IUPAC name of the following compound:

$(CH_3CH_2)_2NCH_3$ **Delhi 2017**

16. Write the IUPAC name of the following compound:

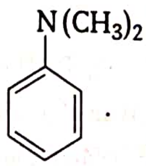
$CH_3NHCH(CH_3)_2$ **Delhi 2017**

17. Write the IUPAC name of the following compound.



Delhi 2013 C

18. Write down the IUPAC name of



NCERT Exemplar

19. Draw the structure of prop-2-en-1-amine.

Or Write the IUPAC name and structure of allyl amine. **All India 2013**

20. Write the IUPAC name of the following compound:

$$CH_3-CH_2-CH_2-CH_2-N\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

All Indian 2017 C

21. Write the main product of the following reaction:

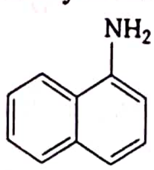
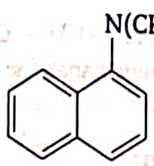
$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2 + NaOH}$$

All India 2013

22. What is the best reagent to convert nitrile to primary amine? **NCERT Exemplar**

SHORT ANSWER Type I Questions

23. Classify the following amines as primary, secondary or tertiary.

(i)  (ii) 

(iii) $(C_2H_5)_2CHNH_2$

(iv) $(C_2H_5)_2NH$ **NCERT Intext**

24. Write the IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines. **NCERT**

(i) $(CH_3)_2CHNH_2$ (ii) $CH_3(CH_2)_2NH_2$

25. Write the IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

(i) $C_6H_5NHCH_3$ (ii) $(CH_3CH_2)_2-N-CH_3$ **NCERT**

26. Write the IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines.

(i) $CH_3NHCH(CH_3)_2$ (ii) $(CH_3)_3CNH_2$ **NCERT**

27. Give the structures of *A*, *B* and *C* in the following reaction.

$$CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$$ **NCERT**

28. Give the structures *A*, *B* and *C* in the following reaction.

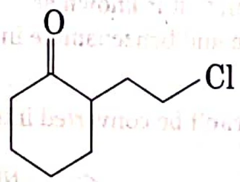
$$CH_3CN \xrightarrow{H_2O/H^+} A \xrightarrow[\Delta]{NH_3} B \xrightarrow{Br_2 + KOH} C$$ **Delhi 2014**

29. How will you convert the following?

(i) Nitrobenzene into aniline

(ii) Ethanoic acid into methanamine **All India 2014**

30. Identify *A* and *B* in the following reaction.

 $\xrightarrow{KCN} A \xrightarrow{H_2/Pd} B$

NCERT Exemplar

31. Name the reaction:

(i) $CH_3CH_2CONH_2 + Br_2 + 4NaOH \longrightarrow CH_3CH_2NH_2 + Na_2CO_3 + 2NaBr$

(ii) $R-X + :NH_3 \xrightarrow[\text{Sealed tube}]{373\text{ K}} R-\overset{+}{N}H_3X^- \underset{}{\overset{NH_3}{\rightleftharpoons}} \underset{1^\circ \text{ amine}}{RNH_2} + NH_4^+X^-$

32. Explain any one method which is used for preparing amine containing one carbon less than the reactant.

SHORT ANSWER Type II Questions

33. (i) Give the structures of different isomeric amines corresponding to the molecular formula, $C_4H_{11}N$.

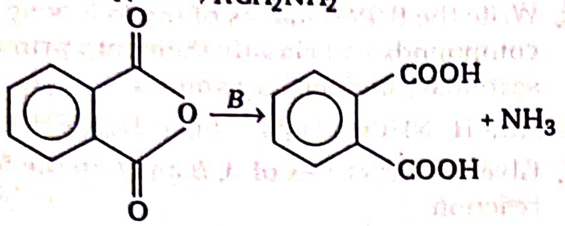
(ii) Write the IUPAC names of all the isomers.

(iii) What type of isomerism is exhibited by different pairs of amines? **NCERT Intext**

34. In the reduction of nitro compounds, why Fe scrap and HCl is preferred over other metals?

35. Name the reagent used in the following reactions.

(i) $R-C\equiv N \xrightarrow{A} RCH_2NH_2$

(ii) 

(iii) $C_6H_5NO_2 + 3H_2 \xrightarrow{C} C_6H_5NH_2 + 2H_2O$

36. Write short notes on the following.

(i) Hofmann bromamide reaction

(ii) Ammonolysis

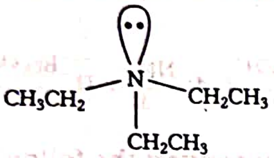
(iii) Gabriel phthalimide synthesis

All India 2013; NCERT

37. Which type of reagent is a good choice for reducing an aryl nitro compound to an amine?

HINTS AND EXPLANATIONS

1. *(b)* Triethylamine is a 3° amine.

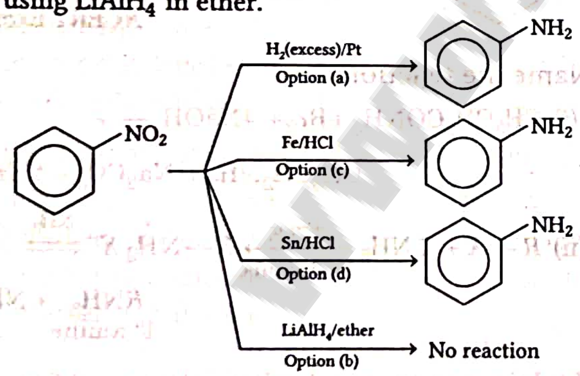


Triethylamine
(3° amine)

2. *(b)* $H_2N-CH_2CH_2NH_2$ is named as ethane-1,2-diamine.

3. *(a)* In aryl amines, when $-NH_2$ group is directly attached to the benzene ring, it is known as aniline in common system and benzenamine in IUPAC system.

4. *(b)* Aryl nitro compound can't be converted into amine using $LiAlH_4$ in ether.

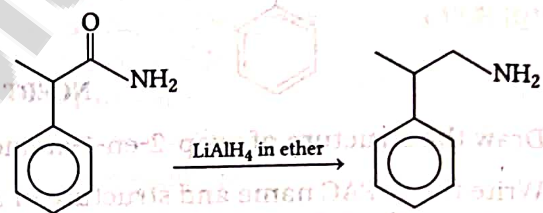


Hence, option (b) is the correct choice.

5. *(b)* The amides on reduction with $LiAlH_4$ yield amine.

$$R-CONH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2NH_2$$

6. *(d)* The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is $LiAlH_4$ in ether. Reaction is as given below



7. *(b)* Propanamide on reaction with bromine in aqueous NaOH gives ethanamine. This reaction is known as Hofmann bromamide degradation reaction. Complete reaction is as follows:

$$\underset{\text{Propanamide}}{CH_3CH_2CONH_2} + \underset{\text{Bromine}}{Br_2} + \underset{\text{Sodium hydroxide}}{4NaOH} \longrightarrow$$

$$\underset{\text{Ethanamine}}{CH_3CH_2NH_2} + \underset{\text{Sodium carbonate}}{Na_2CO_3} + \underset{\text{Sodium bromide}}{2NaBr} + \underset{\text{Water}}{2H_2O}$$

8. *(d)* IUPAC name of product formed by reaction of methyl amine with two moles of ethyl chloride is N - ethyl - N - methyl ethanamine.

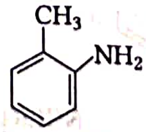
Complete reaction is as follows:

$$\underset{\text{Methyl amine}}{CH_3NH_2} \xrightarrow{C_2H_5Cl} \underset{\text{N-methyl ethanamine}}{CH_3-\overset{H}{\overset{|}{N}}-C_2H_5} \xrightarrow{C_2H_5Cl} \underset{\text{N-ethyl-N-methyl ethanamine}}{H_3C-\overset{C_2H_5}{\overset{|}{N}}-C_2H_5}$$

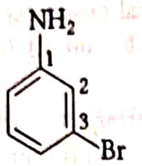
9. Alkaloids and proteins.

10. $\overset{2}{C}H_3-\overset{1}{C}H_2-NH-CH_3$

N-methylethanamine

11. 

2-aminotoluene

12. 

(Primary/1°-amine) 3-bromoaniline

13. $CH_3—\underset{\underset{NH_2}{|}}{CH}—CH_2—CHO$

IUPAC name 3-amino-1-butanal or 3-aminobutanal

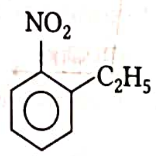
14. Given compound, $H_3C—\underset{\underset{CH_3}{|}}{N}—CH_2CH_3$

IUPAC name N, N-dimethyl ethanamine.

15. Given compound is $H_3CH_2C—\overset{\overset{CH_3}{|}}{N}—CH_2CH_3$

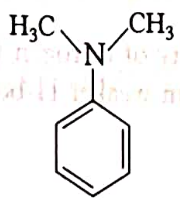
IUPAC Name N-ethyl, N-methylethanamine.

16. The IUPAC name for $CH_3NHCH(CH_3)_2$ is N-methylpropan-2-amine.

17. 

2-ethylnitrobenzene

18. During naming of N-substituted amine, substituted group present at N is added as suffix N-alkyl in IUPAC nomenclature.



N, N-dimethylbenzenamine

19. $\overset{3}{C}H_2=\overset{2}{C}H—\overset{1}{C}H_2NH_2$

Prop-2-en-1-amine

20. N, N-dimethylbutan-1-amine

21. $CH_3—\underset{\underset{O}{\|}}{C}—NH_2 \xrightarrow[\text{Hofmann bromamide reaction}]{Br_2 + 4\,NaOH} CH_3NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

22. The best reagent to reduce nitriles is sodium/alcohol or $LiAlH_4$ and the product of this reduction is primary amine.

23. (i) Primary (ii) Tertiary
(iii) Primary (iv) Secondary

24. (i) Propan-2-amine (1°) (ii) Propanamine (1°)

25. (i) N-methylbenzenamine (2°)
(ii) N-ethyl-N-methylethanamine (3°)

26. (i) N-methylpropan-2-amine (2°)
(ii) 2-methylpropan-2-amine (1°)

27. $\underset{\text{Ethyl iodide}}{CH_3CH_2I} \xrightarrow{NaCN} \underset{\substack{\text{Ethyl cyanide}\\ A}}{CH_3CH_2CN} \xrightarrow[\text{Partial hydrolysis}]{OH^-}$

$\underset{\substack{\text{Propionamide}\\ B}}{CH_3CH_2CONH_2} \xrightarrow{NaOH + Br_2} \underset{\substack{\text{Ethyl amine}\\ C}}{CH_3CH_2NH_2}$

28. $CH_3CN \xrightarrow{H_2O/H^+} \underset{A}{CH_3COOH} \xrightarrow[\Delta]{NH_3}$

$\underset{B}{CH_3CONH_2} \xrightarrow{Br_2 + 4KOH} \underset{C}{CH_3NH_2}$

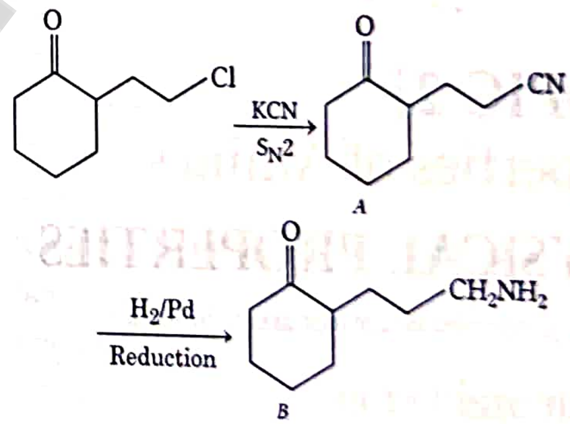
29. **(i) Nitrobenzene into aniline**

$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 3H_2 \xrightarrow[\text{or Fe + HCl}]{Sn + HCl} \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$

(ii) Ethanoic acid into methanamine

$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\text{Ethanoyl chloride}}{CH_3COCl} \xrightarrow{NH_3(\text{excess})}$

$\underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\text{(Hofmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$

30. 

31. Refer to text on page 363.

32. Refer to text on page 363.

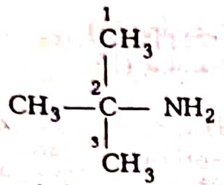
33. (i) and (ii)

Eight isomers of $C_4H_{11}N$ are:

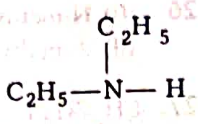
(a) $\overset{4}{C}H_3—\overset{3}{C}H_2—\overset{2}{C}H_2—\overset{1}{C}H_2—NH_2$
Butan-1-amine
(Primary)

(b) $\overset{3}{C}H_3—\overset{\overset{CH_3}{|}}{\overset{2}{C}H}—\overset{1}{C}H_2—NH_2$
2-methyl propan-1-amine
(Primary)

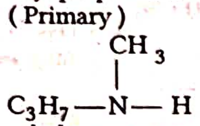
(c) $\overset{4}{C}H_3—\overset{3}{C}H_2—\overset{\overset{\overset{1}{C}H_3}{|}}{\overset{2}{C}H}—NH_2$
Butan-2-amine
(Primary)

(d) 

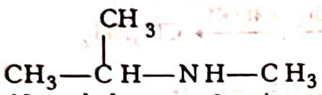
2-methyl propan-2-amine
(Primary)

(e) 

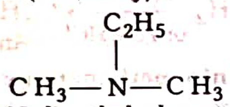
N-ethyl ethanamine
(Secondary)

(f) 

N-methyl propan-1-amine
(Secondary)

(g) 

N-methyl propan-2-amine
(Secondary)

(h) 

N, N-dimethyl ethanamine
(Tertiary)

(iii) Isomerism exhibited by different amines are:

(a) **Chain isomers**, i.e. have different carbon chains, (a) and (b), (c) and (d) [as discussed in part (i) and (ii)]

(b) **Position isomers**, i.e. functional group occupy different positions, (b) and (c), (b) and (d), (a) and (d).

(c) **Metamers**, i.e. different alkyl groups are attached to the same functional group, (e) and (f), (g) and (e).

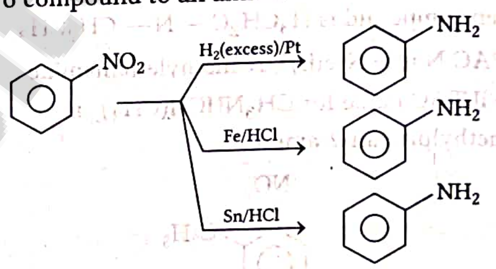
(d) **Functional isomers**, i.e. they have different functional groups. All the three categories (1°, 2° and 3°) of amines are the functional isomers of each other.

34. Refer to text on pages 362 and 363.

35. (i) Refer to text on page 363.
(ii) Refer to text on page 363.
(iii) Refer to text on page 362.

36. Refer to text on page 363.

37. Following reagent are good choice for reducing an aryl nitro compound to an amine.



|TOPIC 2|
Properties of Amines

PHYSICAL PROPERTIES

Physical properties of amines are as follows :

Colour and Odour

Pure amines are colourless but develop colour on keeping in air or on storage due to atmospheric oxidation. The lower aliphatic amines are gases and smell like ammonia. Primary amines with three or more carbon atoms are liquids with fishy odours and higher ones are solid. Aromatic amines are toxic in nature.

Solubility

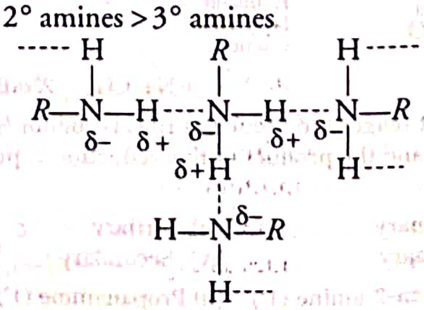
Lower aliphatic amines can form hydrogen bonds with water molecules and hence are soluble in water. Solubility of amines decreases with increase in molar mass due to increase in the hydrophobic part which retard the formation of H-bonds and hence, higher amines containing six or more carbon atoms are insoluble in water.

Since, the electronegativity of nitrogen (3.0) is lower than oxygen (3.5), amines form weaker H-bond than alcohols and carboxylic acids.

Boiling Point

Amines are polar and hence form intermolecular H-bonds and therefore, they have higher boiling points. This intermolecular association depends upon the extent of H-bonding. 1° amines have two, 2° amines have one, while 3° amines have no hydrogen bonded to nitrogen. Therefore, the order of boiling point of amines is:

1° amines > 2° amines > 3° amines.



Intermolecular hydrogen bonding in primary amines

Boiling point of amines, alcohols and alkanes of almost the same molar mass are as shown below:

Comparison of boiling points of amines, alcohols and alkanes of almost similar molecular mass

S.No.	Compound	Molar mass	Boiling point/K
1.	n-$C_4H_9NH_2$	73	350.8
2.	$(C_2H_5)_2NH$	73	329.3
3.	$C_2H_5N(CH_3)_2$	73	310.5
4.	$C_2H_5CH(CH_3)_2$	72	300.8
5.	n-C_4H_9OH	74	390.3

CHEMICAL REACTIONS

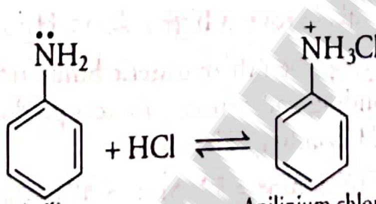
Amines are very reactive due to the difference in electronegativity between nitrogen and hydrogen atoms and due to the presence of unshared pair of electrons over N-atom. The number of hydrogen atoms attached to the N-atom decides the course of reactions of amine, that is why, amines differ in many reactions.

Some of the reactions of amines are described below:

Basic Character of Amines

Amines have an unshared pair of electrons over the nitrogen atom and hence, they behave as Lewis base. They readily react with mineral acids to form soluble salts.

$$R—\ddot{N}H_2 + H—X \rightleftharpoons \underset{\text{(Salt)}}{R—\overset{+}{N}H_3X^-}$$



Aniline Anilinium chloride

The amine salts on treatment with a base (NaOH), regenerate the parent amine.

$$R\overset{+}{N}H_3X^- + \bar{O}H \longrightarrow R\ddot{N}H_2 + H_2O + X^-$$

Amine salts are soluble in water but insoluble in organic solvents like ether. That is why, this reaction is used for the separation of amines from the non-basic organic compounds which are insoluble in water.

Basic character of amine can be better understood in terms of their K_b and pK_b values as explained below:

$$R—\ddot{N}H_2 + H_2O \rightleftharpoons R—\overset{+}{N}H_3 + \bar{O}H$$

$$K = \frac{[R—\overset{+}{N}H_3][\bar{O}H]}{[R—NH_2][H_2O]}$$

or $$K[H_2O] = \frac{[R—\overset{+}{N}H_3][\bar{O}H]}{[R—NH_2]}$$

$$K_b = \frac{[R—\overset{+}{N}H_3][\bar{O}H]}{[R—NH_2]}$$

$$pK_b = -\log K_b$$

Larger the value of K_b or smaller the value of pK_b, stronger is the base.

e.g. K_b $\underset{12.0\times10^{-10}}{p\text{-toluidine}} > \underset{5\times10^{-10}}{m\text{-toluidine}} > \underset{4.2\times10^{-10}}{\text{aniline}} > \underset{2.6\times10^{-10}}{o\text{-toluidine}}$

pK_b $\underset{3.27}{(CH_3)_2NH} > \underset{3.38}{CH_3NH_2} > \underset{4.22}{(CH_3)_3N}$

pK_b values of amines in aqueous phase

Name of amine	pK_b
Methanamine	3.38
N-methylmethanamine	3.27
N,N-dimethylmethanamine	4.22
Ethanamine	3.29
N-ethylethanamine	3.00
N,N-diethylethanamine	3.25
Benzenamine	9.38
Phenylmethanamine	4.70
N-methylaniline	9.30
N,N-dimethylaniline	8.92

Aliphatic amines are stronger bases than ammonia due to $+I$-effect (electron-donating power) of alkyl groups ouring to which electron density on nitrogen atom increases and hence, they can easily donate their electrons.

Aliphatic amine **Ammonia**

$\underset{(+I\text{-effect})}{CH_3 \rightarrow NH_2}$ $H—\ddot{N}—H$ with H below N (no + I- effect)

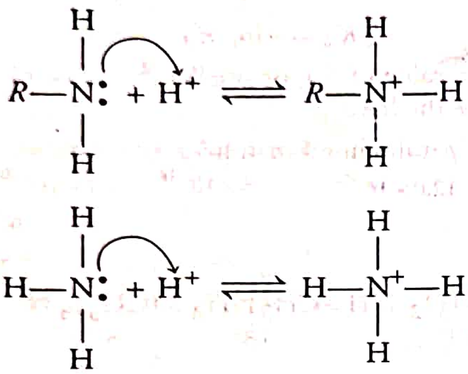
On the other hand, aromatic amines are weaker bases than ammonia due to electron withdrawing nature of aryl group. pK_b values of ammonia is 4.75 and pK_b values of aliphatic amine lies between the range 3 to 4.22.

Structure-Basicity Relationship of Amines

Basic character of amines depends upon the ease for the formation of cation by accepting a proton from acid. The more stable the cation is relative to the amine, more basic is the amine.

Alkanamine versus Ammonia

The reaction of an alkanamine and ammonia with a proton is used to compare their basicity.



Due to electron releasing nature of alkyl group, it pushes electrons towards nitrogen and makes the unshared electron pair more available for sharing with the proton of the acid.

The substituted ammonium ion formed from the amine gets stabilised due to dispersal of the positive charge by the +*I*-effect of alkyl group. Thus, basic nature of amine increases with increase in the number of alkyl group.

Order of basicity of amines in gaseous phase is as follows:

Tertiary amine > Secondary amine > Primary amine > Ammonia

Basicity in Aqueous Phase

Basicity of an amine in aqueous solution depends upon the stability of ammonium cation formed by accepting proton from water. The stability of ammonium cation depends upon the following three factors:

(i) +*I*-effect (alkyl group)

(ii) Solvation effect

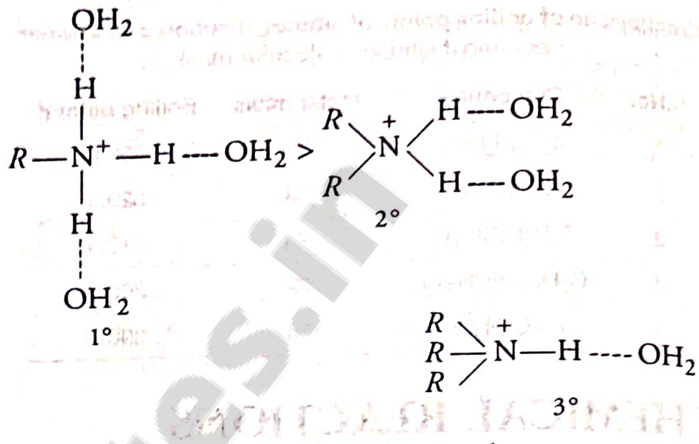
(iii) Steric effects (alkyl groups)

If we consider the first case, then as we increase the size of alkyl group, +*I*-effect increases and the positive charge of ammonium cation gets dispersed more easily. Therefore, the order of basicity is

$$3° \text{ amine} > 2° \text{ amine} > 1° \text{ amine}$$

Substituted ammonium cation also gets stabilised by solvation with water molecules. The greater the size of ion, lesser will be the solvation and the less stabilised is the ion.

Decreasing order of extent of H-bonding in water and order of stability of ion by solvation



If we consider second and third cases, then greater the number of H-atoms on the N-atom, greater will be the H-bonding and, hence more stable is the ammonium cation. When ammonium cation is derived from 3° amine, stability further decreases, due to steric repulsion to H-bonding. So, order of stability is:

$$1° \text{ amine} > 2° \text{ amine} > 3° \text{ amine}$$

So the two cases arise as:

Case I If we combine these 3 factors and if the alkyl group is small, i.e. CH_3, then there is no steric hindrance to H-bonding and, hence H-bonding predominates over +*I*-effect. Since, all these effects are favourables for 2° amine. Therefore,

$$2° \text{ amine} > 1° \text{ amine} > 3° \text{ amine}$$

Case II If the alkyl group is bigger than CH_3 group, i.e. C_2H_5, then there is steric hindrance to H-bonding and hence, + *I*-effect predominates over H-bonding. Therefore,

$$2° \text{ amine} > 3° \text{ amine} > 1° \text{ amine}$$

There is a suitable interplay of the inductive effect, solvation effect and steric hindrance of alkyl group which decides the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of ethyl substituted amines and methyl substituted amines in aqueous solution is as follows:

$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

Arylamines versus Ammonia

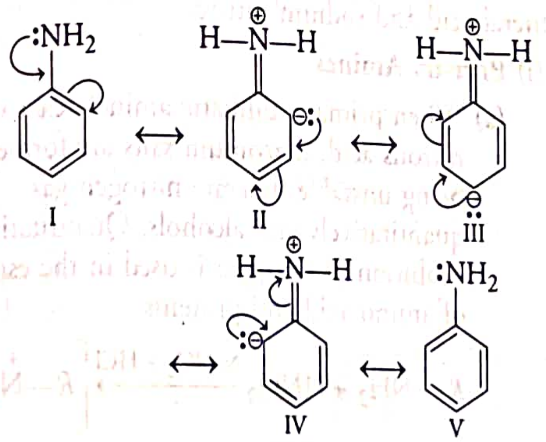
pK_b value of aniline is quite high due to the following reasons:

(i) As, NH_2 group is directly attached to benzene ring, the lone pair of electrons gets delocalised inside the

benzene ring and thus, it is less available for protonation. Therefore, aromatic amines (aniline) are weaker bases than ammonia.

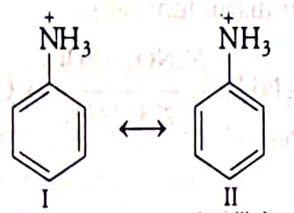
(ii) If we consider the resonating structures, then we know that greater the number of resonating structures, greater is the stability.

The resonating structures of aniline are as follows:



Resonating structures of aniline

In anilinium ion, there are two resonating structures, therefore, it is less stable than aniline (five resonating structures).



Resonating structures of anilinium ion

(iii) In case of substituted aniline, electron releasing groups like $-CH_3$, $-OCH_3$, $-NH_2$ increase the basic strength and electron withdrawing groups like $-NO_2$, $-X$, $-COOH$ decrease the basic strength.

Alkylation

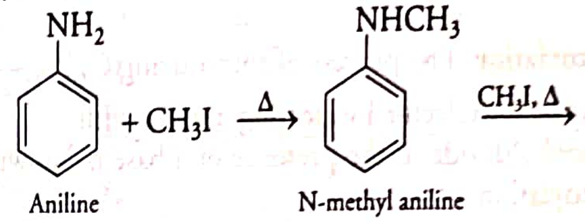
Amines undergo alkylation on reaction with alkyl halides.

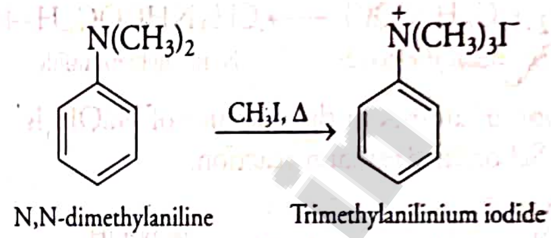
$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + \underset{\text{Ethyl bromide}}{CH_3CH_2Br} \longrightarrow \underset{\text{Diethylamine}}{(CH_3CH_2)_2NH} + HBr$$

$$\underset{\text{Diethylamine}}{(CH_3CH_2)_2NH} + \underset{\text{Ethyl bromide}}{CH_3CH_2Br} \longrightarrow \underset{\text{Triethyl amine}}{(CH_3CH_2)_3N} + HBr$$

$$\xrightarrow{CH_3CH_2Br} \underset{\text{Tetraethylammonium bromide}}{(CH_3CH_2)_4\overset{+}{N}Br^-}$$

Similarly,



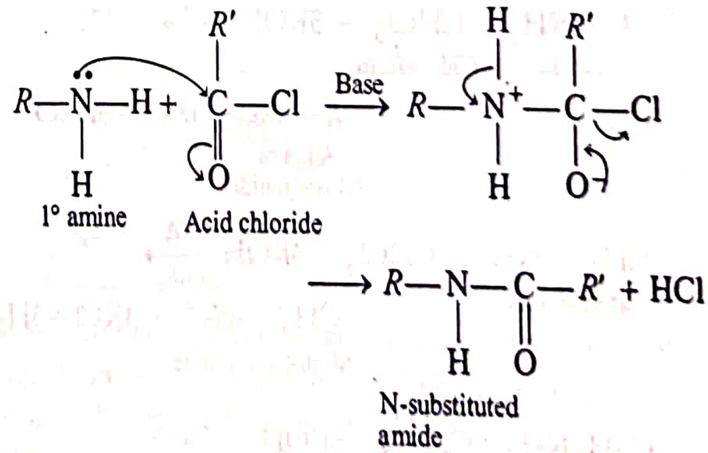


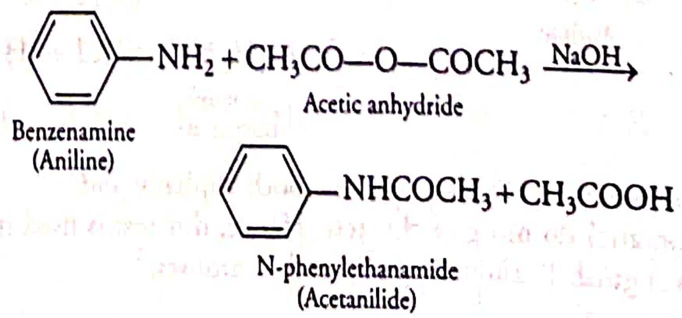
The process of conversion of a 1° amines into quaternary ammonium salt is called Hofmann exhaustive alkylation.

Acylation

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is considered as replacement of hydrogen atom of $-NH_2$ or $>NH$ group by acyl group. This reaction is known as acylation.

The reaction is carried out in the presence of a base stronger than amine like pyridine, which removes HCl so formed and shifts the equilibrium towards right hand side. The product obtained by acylation reactions is known as amides.

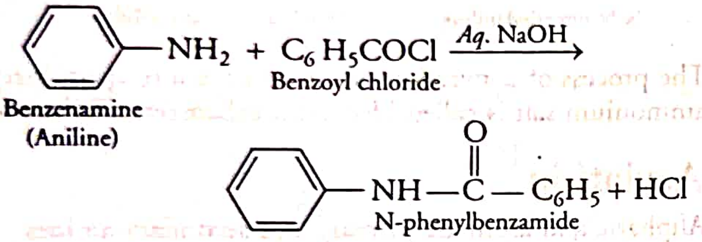




Benzoylation The process of introducing $C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-$ group in a molecule by treating amines with benzoyl chloride in the presence of a base is known as benzoylation.

$$\underset{\text{Methanamine}}{CH_3NH_2} + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \longrightarrow \underset{\text{N-methylbenzamide}}{CH_3NHCOC_6H_5} + HCl$$

Benzoylation of amines in the presence of NaOH is known as Schotten-Baumann reaction.



Note At room temperature, amines react with carboxylic acid to form corresponding salts.

Carbylamine Reaction

Primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which have foul smell. This reaction is called carbylamine reaction or isocyanide test. These reactions are used to test primary amines.

In general,

$$\underset{\text{Amine}}{R-NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Alkyl or}\\ \text{aryl isocyanide}}}{R-NC} + 3KCl + 3H_2O$$

$$\underset{\text{Methylamine}}{CH_3-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Methyl isocyanide}}{CH_3-NC} + 3KCl + 3H_2O$$

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\substack{\text{Phenyl}\\ \text{isocyanide}}}{C_6H_5NC} + 3KCl + 3H_2O$$

Secondary and tertiary amines (both aliphatic and aromatic) do not give this test. Hence, this test is used to distinguish 1° amine from 2° and 3° amines.

IDENTIFICATION OF 1°, 2° AND 3° AMINES

(I) Reaction with Nitrous Acid

Primary, secondary and tertiary amines react differently with nitrous acid which is prepared in situ from a mineral acid and sodium nitrite.

(i) **Primary Amines**

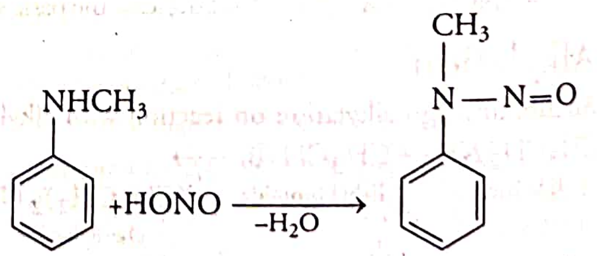
(a) When primary aliphatic amines react with nitrous acid, diazonium salts are formed which being unstable, liberate nitrogen gas quantitatively and alcohols. Quantitative evolution of nitrogen is used in the estimation of amino acid and proteins.

$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} \left[R-\overset{+}{N}_2\overset{-}{Cl}\right] \xrightarrow{H_2O} \underset{\text{Alcohols}}{R-OH} + N_2\uparrow + HCl$$

(b) Aromatic primary amines also react with nitrous acid at low temperatures (273-278 K), to form diazonium salts.

$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[273\text{-}278\text{ K}]{NaNO_2 + 2HCl} \underset{\substack{\text{Benzene diazonium}\\ \text{chloride}}}{C_6H_5-\overset{+}{N}_2\overset{-}{Cl}} + NaCl + 2H_2O$$

(ii) **Secondary Amines** Secondary amines react with nitrous acid to form a yellow green oily layer of N-nitroso amines. This reaction is also called Liebermann's nitrosoamine test.



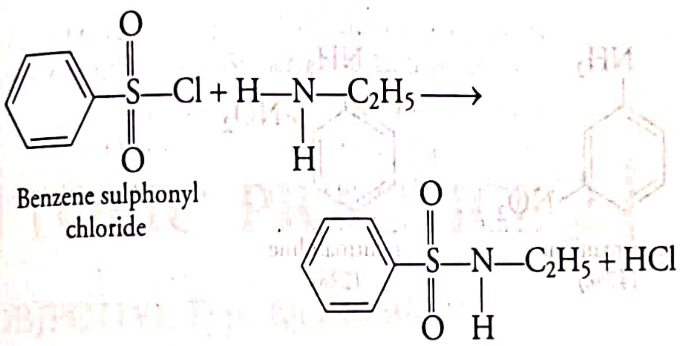
N-Nitroso-N-methyl aniline
(Yellow oil liquid)

(iii) **Tertiary Amines** Tertiary amines readily dissolve in nitrous acid forming crystalline trialkyl ammonium nitrite.

$$R_3N + HNO_2 \longrightarrow \underset{\substack{\text{Trialkyl ammonium}\\ \text{nitrite}}}{R_3\overset{+}{N}\;HNO_2^-}$$

(II) Reaction with Aryl Sulphonyl Chloride

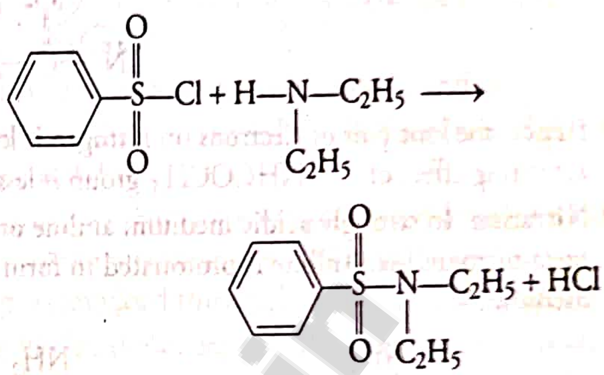
(i) Primary amine when reacts with benzene sulphonyl chloride (Hinsberg's reagent), it yields N-ethylbenzene sulphonamide. Hydrogen attached to nitrogen is strongly acidic due to the presence of strong electron withdrawing sulphonyl group, hence, it is soluble in alkali.



Benzene sulphonyl chloride

N-ethylbenzene sulphonamide (Soluble in alkali)

(ii) Secondary amine when reacts with benzene sulphonyl chloride, it yields N,N-diethylbenzene sulphonamide. Since, it does not have any H-atom attached to N-atom, it is not acidic and hence, insoluble in alkali.



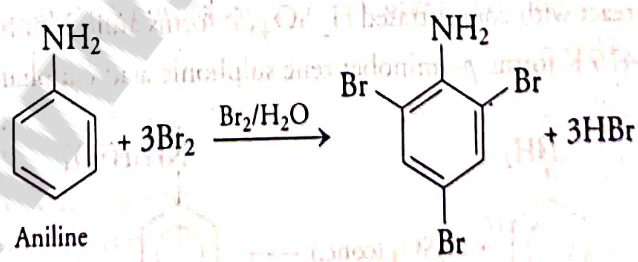
N,N-diethylbenzene sulphonamide (Insoluble in alkali)

(iii) Tertiary amines do not react with benzene sulphonyl chloride.
This property of amine reacting with benzene sulphonyl chloride in a different way is used for the distinction of 1°, 2° and 3° amines and also for the separation of a mixture of amines. Now-a-days, benzene sulphonyl chloride is replaced by *p*-toluene sulphonyl chloride.

Electrophilic Substitution Reactions

In aniline, electron density at *ortho* and *para*-positions with respect to $—NH_2$ group is high Therefore, this group is *ortho* or *para*-directing and a powerful activating group.

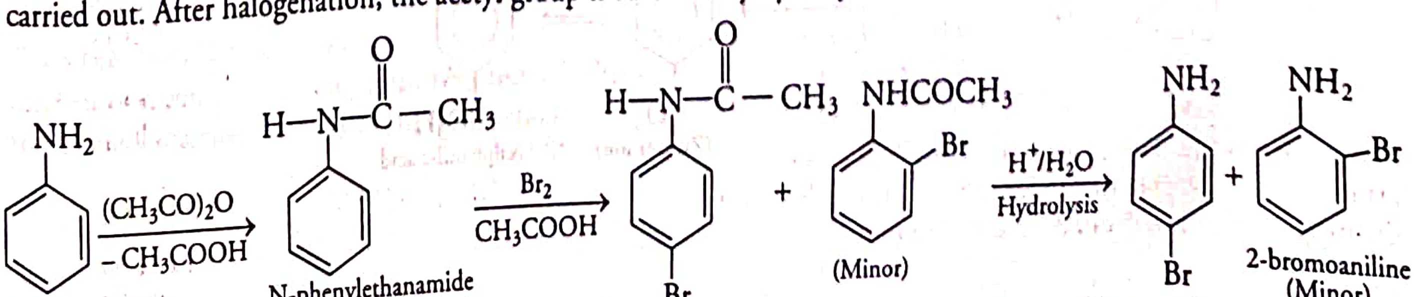
(i) **Halogenation** (Bromination) In the absence of catalyst, aniline on treatment with bromine water forms 2, 4, 6-tribromoaniline.



Aniline

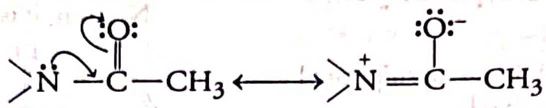
2,4,6-tribromoaniline

The main problem encountered during electrophilic substitution reaction of aromatic amine is that they have very high reactivity towards substitution at *ortho* and *para*-positions. In order to get monohalogenated derivative, the activating effect of $—NH_2$ group was controlled by acetylation with acetic anhydride and then halogenation is carried out. After halogenation, the acetyl group is removed by hydrolysis.



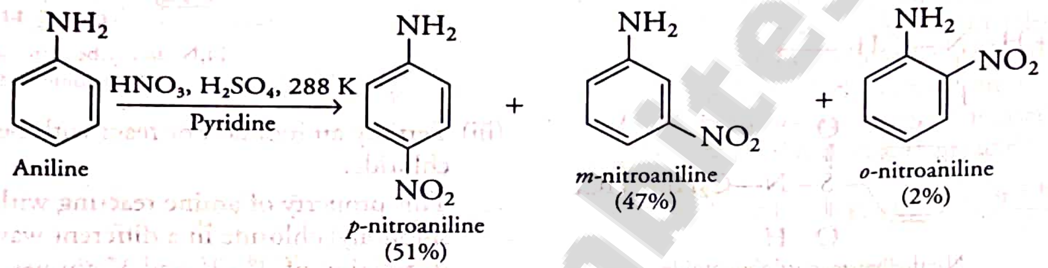
Aniline; N-phenylethanamide (Acetanilide); (Major); (Minor); 4-bromoaniline (Major); 2-bromoaniline (Minor)

The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:

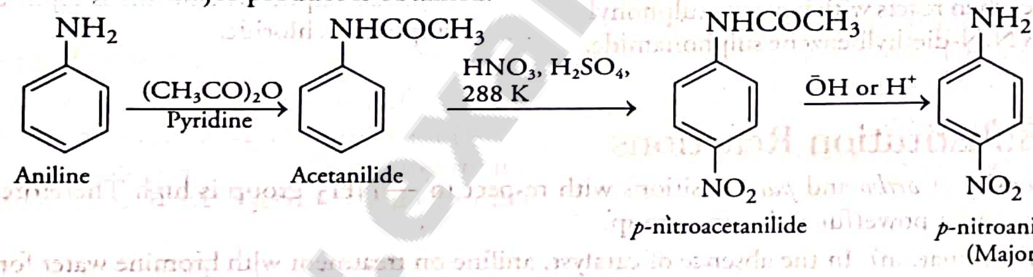


Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance, therefore activating effect of $>NHCOCH_3$ group is less than that of amine group.

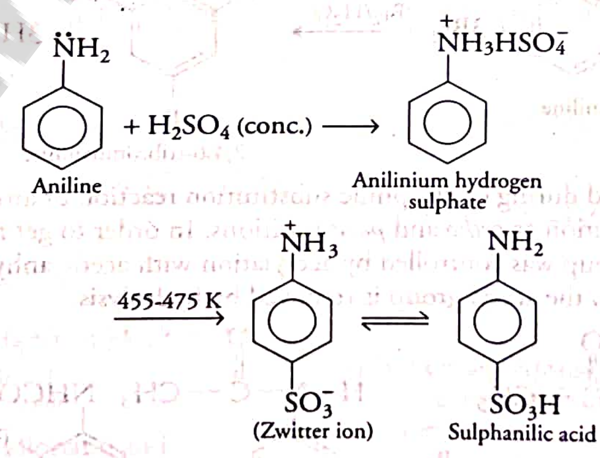
(ii) Nitration In strongly acidic medium, aniline on nitration gives a mixture of *ortho*, *para* and significant amount of *meta*-nitroaniline. Aniline is protonated to form anilinium ion which is a *m*-directing group under strongly acidic medium.



By protecting the $—NH_2$ group by acetylation with acetic anhydride, the reaction can be controlled and only *p*-nitro derivative as the major product is obtained.

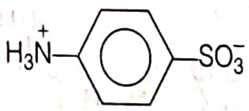


(iii) Sulphonation Aniline when react with concentrated H_2SO_4, it forms anilinium hydrogen sulphate which on heating with H_2SO_4 at 455-475 K forms *p*-aminobenzene sulphonic acid (sulphanilic acid).



Note
Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with anhydrous $AlCl_3$, the Lewis acid, which is used as a catalyst. As a result, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

Zwitter ion The ion which contains both positive and negative charges and also contains acidic and basic groups in the same molecule is known as Zwitter ion. e.g.



Structure of Zwitter ion

Uses of Amines

(i) Aliphatic amines are used as solvents and intermediates in the manufacture of drugs.
(ii) They are used as reagents in organic synthesis.
(iii) Aromatic amines are used for the formation of polymers, dyes and drugs.
(iv) Quaternary salts of amines are formed from long chain tertiary amines which are used as detergents, e.g. *n*-hexadecyl trimethylammonium chloride.
(v) N, N-dimethylaniline (DMA) is used in the preparation of dyes.

TOPIC PRACTICE 2

OBJECTIVE Type Questions

1. Choose the correct order of the boiling point of amines.
(a) Primary > secondary > tertiary
(b) Secondary > tertiary > primary
(c) Tertiary > primary > secondary
(d) Tertiary > secondary > primary

2. Amines on treatment with acids yield salt because they are
(a) basic in nature (b) acidic in nature
(c) amphoteric in nature (d) None of these

3. Amongst the following, the strongest base in aqueous medium is ....
(a) CH_3NH_2 (b) $NCCH_2NH_2$
(c) $(CH_3)_2NH$ (d) $C_6H_5NHCH_3$

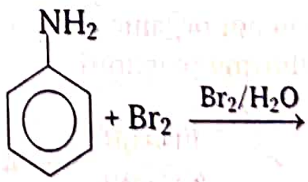
4. Name the product(s) formed during the reaction of primary aliphatic amines with nitrous acid at room temperature?
(a) $RN_2^+Cl^-$ (b) ROH
(c) Both (a) and (b) (d) None of the above

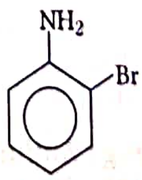
5. N-methylbenzamide is formed when methanamine reacts with benzoyl chloride. This reaction is known as
(a) benzoylation (b) Hinsberg test
(c) Schmidt reaction (d) Curtius reaction

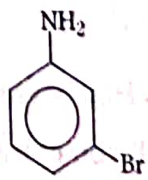
6. $-NH_2$ group in the aniline is activating group and proceed reaction at
(a) only *para* position (b) only *ortho* position
(c) *meta* position (d) Both (a) and (b)

7. Which of the following reactions is/are electrophilic substitution?
(a) Bromination of aniline
(b) Nitration of aniline
(c) Sulphonation of aniline
(d) All of the above

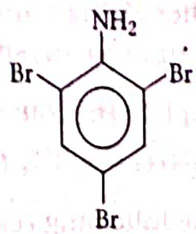
8. Which of the following products is formed in the given reaction?



(a) 

(b) 

(c) 

(d) 

VERY SHORT ANSWER Type Questions

9. Consider the following statement in considering whether amine is 1°, 2° or 3°. "The amine is gaseous and smells like ammonia".

10. Why does the higher aliphatic amines are not soluble in water?

11. Arrange the following compounds in the increasing order of basic strength.
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$ **All India 2014**

12. Arrange the following compounds in the increasing order of dipole moment.
$CH_3CH_2CH_3$, $CH_3CH_2NH_2$, CH_3CH_2OH

13. Give reason why amines are reactive?

14. In the following reaction, which species behave as a Lewis base?

$$R-\ddot{N}H_2 + H-X \rightleftharpoons R-\overset{+}{N}H_3X^-$$

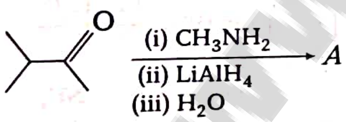
15. What is the role of pyridine in the acylation reaction of amines? **NCERT Exemplar**

16. Complete the following reaction.
$CH_3CH_2NH_2 + CHCl_3 + \text{alc. } 3KOH \longrightarrow$ **All India 2013**

17. Give the chemical test to distinguish between the following pair of compounds, ethylamine and dimethylamine. **All India 2019, Delhi 2013 C**

18. In this reaction, $RNH_2 \xrightarrow{HNO_2} A + B + C\uparrow$
Name the gas C.

19. What is the major organic compound A, formed from the following reaction?

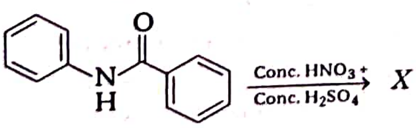


20. What is Hinsberg reagent?

21. How will you convert the following? Aniline into N-phenylethanamide (write the chemical equations involved) **All India 2014**

22. Complete the following reaction. **NCERT**
$C_6H_5NH_2 + H_2SO_4 \text{ (conc.)} \longrightarrow$

23. In the following reaction,

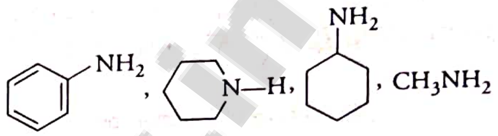


what is the structure of product X?

SHORT ANSWER Type I Questions

24. Arrange the following in the order of their increasing basicity : p-toluidine, N, N-dimethyl-p-toluidine, p-nitroaniline, aniline

25. Write the decreasing order of the following Bronsted bases.



26. Give reasons for the following.
(i) pK_b of aniline is more than that of methylamine.
(ii) Ethylamine is soluble in water whereas aniline is not. **NCERT**

27. Complete the following acid-base reactions and name the products.
(i) $CH_3-CH_2-CH_2-NH_2 + HCl \longrightarrow$
(ii) $(C_2H_5)_3N + HCl \longrightarrow$ **NCERT Intext**

28. Write short notes on the following:
(i) Acylation
(ii) Carbylamine reaction **NCERT**

29. Why is NH_2 group of aniline acetylated before carrying out nitration? **NCERT Exemplar**

30. Write the chemical reaction of aniline with benzoyl-chloride and also write the name of the product obtained. **NCERT Intext**

31. Complete the following reactions.
(i) $C_6H_5NH_2 + CHCl_3 + \text{alc. } 3KOH \longrightarrow$
(ii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\text{ K}]{HNO_2} B$ **NCERT**

32. How will you convert
(i) Nitromethane into dimethylamine?
(ii) Propanoic acid into ethanoic acid? **NCERT**

33. Account for the following.
(i) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
(ii) Aniline does not undergo Friedel-Crafts reaction. **All India 2019, Delhi 2014; NCERT**

34. Benzylamine may be alkylated as shown in the following equation.
$C_6H_5CH_2NH_2 + R-X \longrightarrow C_6H_5CH_2NHR$
Can you predict the 'R' through which S_N1 mechanism can be shown?

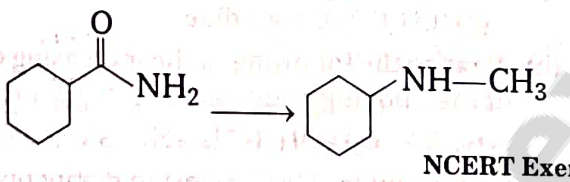
35. $C_5H_{13}N$ reacts with HNO_2 to give an optically active alcohol. What is this compound? Give its IUPAC name.

36. Complete the following reactions.
(i) $C_6H_5NH_2 + 3Br_2(aq) \longrightarrow$
(ii) $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow$
All India 2013; NCERT

37. Write the structures of A, B and C in the following reactions
(i) $C_6H_5—CONH_2 \xrightarrow{Br_2/aq.KOH} A \xrightarrow{NaNO_2,HCl} B \xrightarrow{KI} C$
(ii) $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{CHCl_3 + alc.KOH} C$

38. Give one chemical test to distinguish between the following pairs of compounds.
(i) Aniline and benzylamine
(ii) Aniline and N-methyl aniline
All India 2010; NCERT

39. Suggest a route by which the following conversion can be accomplished.



NCERT Exemplar

SHORT ANSWER Type II Questions

40. Arrange the following in increasing order of property specified: **CBSE SQP 2021**
(i) Aniline, ethanamine, 3-ethylethanamine (solubility in water)
(ii) Ethanoic acid, ethanamine, ethanol (boiling point)
(iii) Methanamine, N, N- dimethylmethanamine and N-methylmethanamine (basic strength in aqueous phase).

41. Arrange the following
(i) in the decreasing order of basic strength in gas phase
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3.
(ii) in the increasing order of boiling point
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$.
NCERT; All India 2014
(iii) in the increasing order of solubility in water
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$. **All India 2014**

42. Arrange the following
(i) in the decreasing order of pK_b values $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$.
(ii) in the increasing order of basic strength $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2.
(iii) In the increasing order of basic strength.
(a) Aniline, p-nitroaniline and p-toluidine
(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$
NCERT; All India 2011; Foreign 2009

43. Arrange the following in the increasing order of their basic strength.
(i) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$
(ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$
(iii) CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$ **NCERT Intext; All India 2011**

44. Give reasons for the following.
(i) Aniline does not undergo Friedel-Crafts reaction.
(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.
(iii) Primary amines have higher boiling point than tertiary amines. **All India 2016, 14**

45. Draw the structures of different isomers corresponding to the molecular formula, C_3H_9N. Write the IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid. **NCERT Intext**

46. (i) Give a chemical test to distinguish between N-methylethanamine and N,N-dimethyl ethanamine. **CBSE SQP 2021**
(ii) Write the reaction for catalytic reduction of nitrobenzene followed by reaction of product so formed with bromine water.
(iii) Out of butan-1-ol and butan-1-amine, which will be more soluble in water and why?

47. How will you convert
(i) ethanamine into methanamine?
(ii) ethanoic acid into propanoic acid?
(iii) methanamine into ethanamine? **NCERT**

48. How will you convert
(i) ethanoic acid into methanamine?
(ii) hexane nitrile into 1-aminopentane?
(iii) methanol into ethanoic acid? **NCERT**

49. Give the structures of *A*, *B* and *C* in the following reactions.

(i) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^\circ C]{HNO_2} C$

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

All India 2014; NCERT

50. Convert the following. **CBSE SQP (Term II)**

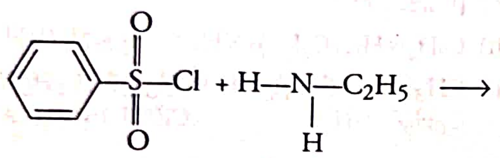
(i) Phenol to N-phenylethanamide

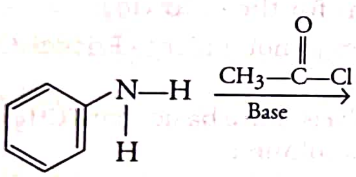
(ii) Chloroethane to methanamine

(iii) Propane nitrile to ethanol

51. Write the main products of the following reactions.

(i) $CH_3CH_2NH_2 \xrightarrow[(0^\circ C)]{HNO_2}$

(ii) 

(iii) 

All India 2013; Delhi 2013; NCERT

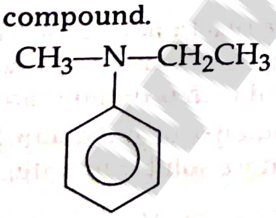
52. What happens when reactions **CBSE SQP Term-II**

(i) N-ethyl ethanamine reacts with benzene sulphonyl chloride ?

(ii) benzyl chloride is treated with ammonia followed by the reaction with chloromethane ?

(iii) Aniline reacts with chloroform in the presence of alcoholic potassium hydroxide.

53. (i) Write the IUPAC name for the following organic compound. **CBSE SQP Term-II**



(ii) Complete the following.

$C_6H_5NO_2 \xrightarrow{Sn/HCl} A \xrightarrow{Br_2/H_2O} B \xrightarrow[273\text{-}278\ K]{NaNO_2/HCl} C \xrightarrow[\Delta]{HBF_4} D$

54. Account for the following.

(i) Although, amino group is *o*-and *p*-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.

(ii) Gabriel phthalimide synthesis is preferred for synthesising primary amines. **NCERT**

55. Give reasons for the following.

(i) Acetylation of aniline reduces its activation effect.

(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$.

(iii) Although $—NH_2$ is *o*/*p*-directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline. **All India 2017; Delhi 2017**

56. Account for the following. **CBSE SQP Term-II**

(i) Aniline cannot be prepared by the ammonolysis of chlorobenzene under normal conditions.

(ii) N-ethylethanamine boils at 329.3K and butanamine boils at 350.8 K, although both are isomeric in nature.

(iii) Acylation of aniline is carried out in the presence of pyridine.

LONG ANSWER TYPE QUESTIONS

57. (i) Write the structure of main products when aniline reacts with the following reagents :

(a) Br_2 water (b) HCl

(c) $(CH_3CO)_2O$/pyridine

(ii) Arrange the following in the increasing order of their boiling point :

$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$

(iii) Give a simple chemical test to distinguish between the following pair of compounds $(CH_3)_2NH$ and $(CH_3)_3N$ **Delhi 2015**

58. Answer the following questions:

(i) The compound of $A(C_3H_9N)$ reacts with benzene sulphonyl chloride to give a solid, insoluble in alkali. Identify '*A*'.

(ii) Outline a synthesis of *p*-bromonitrobenzene from benzene in two steps.

59. An aromatic compound '*A*' of molecular formula $C_7H_6O_2$, undergoes a series of reactions as shown below. Write the structures of *A*, *B*, *C*, *D* and *E* in the following reactions.

$$\underset{A}{(C_7H_6O_2)} \xrightarrow{NH_3/Heat} C_6H_5CONH_2 \xrightarrow{LiAlH_4/Ether} D$$

$$C_6H_5CONH_2 \xrightarrow{Br_2 + NaOH} B \xrightarrow{(CH_3CO)_2O} C$$

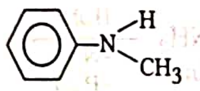
$$B \xrightarrow{Br_2/(aq)} E$$

HINTS AND EXPLANATIONS

1. *(a)* Order of boiling points of isomeric amines is as follows

Primary > secondary > tertiary

2. *(a)* Amines being basic in nature forms salt on treatment with acids.

3. *(c)*	Compound	Factors responsible for basic character are
(a)	CH_3-NH_2	Inductive effect (+ *I*)
(b)	$NC-CH_2-NH_2$	Inductive effect (− *I*)
(c)	$(CH_3)_2NH$	Inductive effect (+ *I*) and Solvation
(d)		− *I* effect and resonance

Since, + *I* effect and solvation increases basic character while −*I* effect and resonance decreases basic character. Hence, correct choice is (c).

4. *(b)* Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, forms alcohol and liberate nitrogen gas quantitatively.

$$R{-}NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [RN_2^+Cl^-]$$

$$\xrightarrow{H_2O} ROH + N_2\uparrow + HCl$$

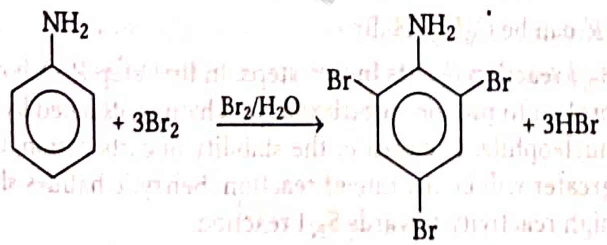
5. *(a)* Amines react with benzoyl chloride to give N-methyl benzamide. This reaction is known as benzoylation.

$$\underset{\text{Methanamine}}{CH_3NH_2} + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \longrightarrow \underset{\text{N-methylbenzamide}}{CH_3NHCOC_6H_5} + HCl$$

6. *(d) Ortho* and *para*-positions to the NH_2 group have high electron density. Thus, NH_2 group is *ortho* and *para*-directing and a powerful activating group.

7. *(d)* Bromination, nitration and sulphonation of aniline are electrophilic substitution reactions.

8. *(d)* Aniline reacts with bromine water at room temperature to give white precipitate of 2, 4, 6-tribromoaniline.



2, 4, 6-tribromoaniline

9. Primary amine

10. Because thay have no hydrogen bond.

11. Increasing order of basic strength

$$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$$

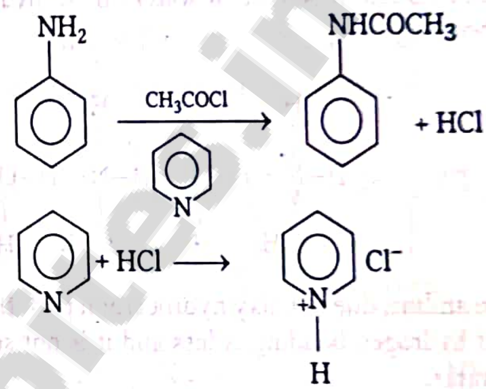
12. As the bond polarity increases, dipole moment increases and hence, order is

$$CH_3CH_2CH_3 < CH_3CH_2NH_2 < CH_3CH_2OH$$

13. Amines are reactive due to the difference in electronegativity between hydrogen and nitrogen atom.

14. Primary amine

15. Pyridine being a base, is used to remove the side product, i.e. HCl from reaction mixture.

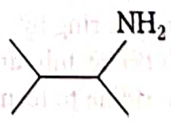


16. $CH_3CH_2NH_2 + CHCl_3 + 3KOH\ (\text{alc.})$

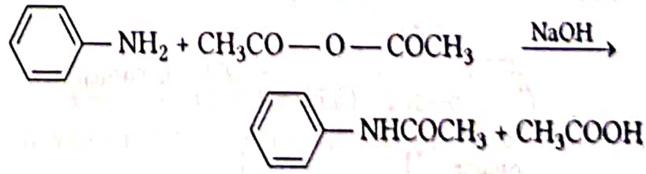
$$\xrightarrow{\Delta} \underset{\text{Ethyl isocyanide}}{CH_3CH_2{-}N \overset{\rightarrow}{=} C} + 3KCl + 3H_2O$$

17. Ethylamine gives carbylamine test, i.e. on treatment with alcoholic KOH and chloroform, followed by heating, it gives offensive odour of ethyl isocyanide. Dimethylamine does not give this test.

18. Nitrogen gas

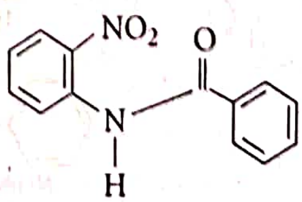
19. 

20. Benzene sulphonyl chloride ($C_6H_5SO_2Cl$) is known as Hinsberg reagent. It is used to distinguish between primary, secondary and tertiary amines.

21. 

22. $C_6H_5NH_2 + H_2SO_4(\text{Conc.}) \longrightarrow C_6H_5\overset{+}{N}H_3HSO_4^-$

$$\xrightarrow{455-475K} C_6H_5NH_2SO_3H$$

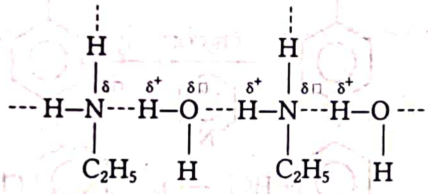
23. 

24. *p*-nitroaniline < aniline < *p*-toluidine < N,N-dimethyl *p*-toluidine.

25. Due to delocalisation of a lone pair of electrons present on the N-atom into the benzene ring, $C_6H_5NH_2$ is weakest base.

26. (i) In aniline, the electron pair on nitrogen atom is involved in conjugation with ring and is less available for protonation than that in methylamine. Therefore, pK_b value of aniline is more than that of methylamine and aniline is less basic (as higher the pK_b value, weaker is the base).

(ii) Ethylamine is soluble in water due to hydrogen bonding.



In aniline, due to bulky hydrocarbon part, the extent of hydrogen bonding is less and it is not soluble in water.

27. (i) $CH_3—CH_2—CH_2—\ddot{N}H_2 + H—Cl \longrightarrow$
n-propylamine

$CH_3—CH_2—CH_2—\overset{+}{N}H_3Cl^-$
n-propyl ammonium chloride

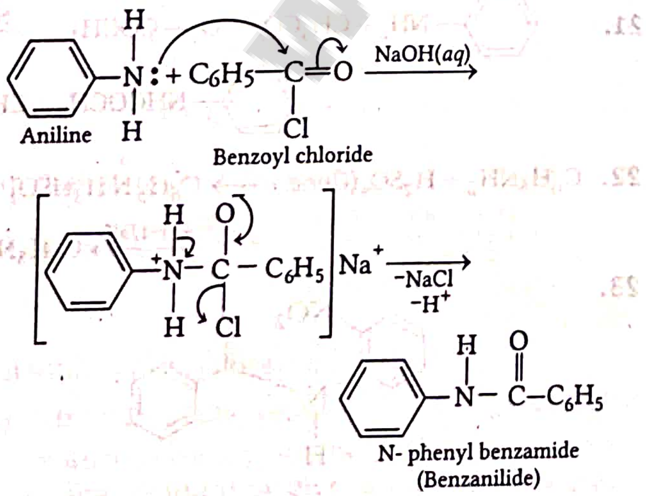
(ii) $(C_2H_5)_3\ddot{N} + H—Cl \longrightarrow (C_2H_5)_3\overset{+}{N}HCl^-$
Triethylamine → Triethylammonium chloride

28. Refer to text on pages 371 and 372.

29. In order to check the activation of benzene ring by amino group, first it is acetylated with acetic anhydride or acetyl chloride in the presence of pyridine to form acetanilide which can be further nitrated easily by nitrating mixture.

For reaction, refer to text on page 373 and 374.

30. The entire reaction sequence can be written as,



31. (i) $C_6H_5NH_2 + CHCl_3 + \text{alc. } 3KOH \xrightarrow{\Delta} C_6H_5NC + 3KCl + H_2O$

(ii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} \underset{(A)}{C_6H_5NH_2} \xrightarrow[273\,K]{HNO_2} \underset{(B)}{C_6H_5\overset{+}{N}_2\overset{-}{Cl}}$

32. Nitromethane into dimethylamine

(i) $\underset{\text{Nitromethane}}{CH_3NO_2} \xrightarrow[{[H]}]{Sn/HCl} \underset{\text{Aminomethane}}{CH_3NH_2} \xrightarrow{CHCl_3/KOH}$

$\underset{\text{Methyl isocyanide}}{CH_3NC} \xrightarrow[{[H]}]{Na/C_2H_5OH} \underset{\text{Dimethylamine}}{CH_3NHCH_3}$

(ii) Propanoic acid into ethanoic acid

$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow{NH_3/\text{Heat}} \underset{\text{Propanamide}}{CH_3CH_2CONH_2}$

$\xrightarrow{Br_2/KOH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO}$

$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[{[O]}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Ethanal}}{CH_3CHO}$

$\xrightarrow[{[O]}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Ethanoic acid}}{CH_3COOH}$

33. (i) Methylamine being more basic than water, accepts a proton from water and OH^- ions are produced which further reacts with ferric ion to give brown ppt. of hydrated ferric oxide.

$\underset{\text{Methylamine}}{CH_3\ddot{N}H_2} + H—OH \longrightarrow CH_3\overset{+}{N}H_3 + OH^-$

$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$

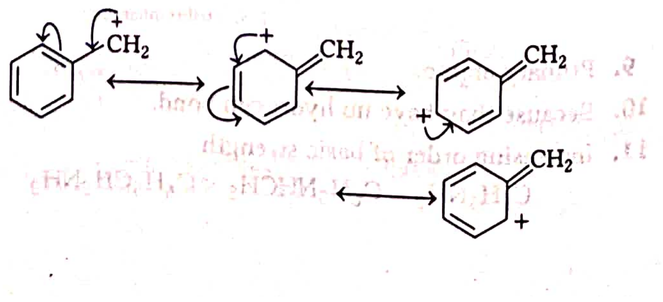
$2Fe^{3+} + 6OH^- \longrightarrow 2Fe(OH)_3$ or $\underset{\text{Hydrated ferric oxide (Brown ppt.)}}{Fe_2O_3 \cdot 3H_2O}$

(ii) Aniline does not undergo Friedel-Crafts reaction as it react with $AlCl_3$ to form a complex. So, further reaction does not takes place.

$\underset{\substack{\text{Aniline}\\ \text{(Lewis base)}}}{C_6H_5\ddot{N}H_2} + \underset{\text{(Lewis acid)}}{AlCl_3} \longrightarrow \underset{\text{(Complex)}}{[C_6H_5NH_2]^+[AlCl_3]^-}$

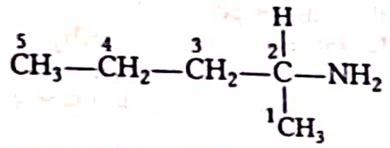
34. '*R*' can be $C_6H_5CH_2Br$

S_N1 reaction occurs in two steps. In first step *R*—*X* bond is broken to produce a carbocation which is attacked by nucleophile. The greater the stability of carbocation, the greater will be the rate of reaction. Benzylic halides show high reactivity towards S_N1 reaction.



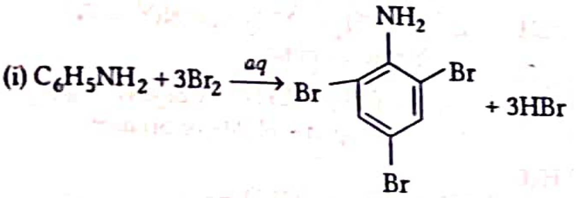
35. HNO_2 reacts with $C_5H_{13}N$ to give an alcohol, means the compound is primary amine. $C_5H_{13}N$ means $C_5H_{11}NH_2$ (primary amine).

Optically active alcohol means $C_5H_{11}OH$ segment contain a chiral carbon.



Pentan-2-amine

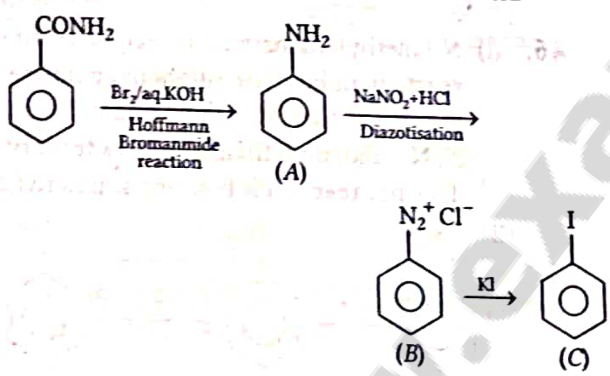
36. (i)



(ii) $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow$
Aniline Ethanoic anhydride

$H_5C_6NHCOCH_3 + CH_3COOH$
N-phenylethanamide or acetanilide Ethanoic acid

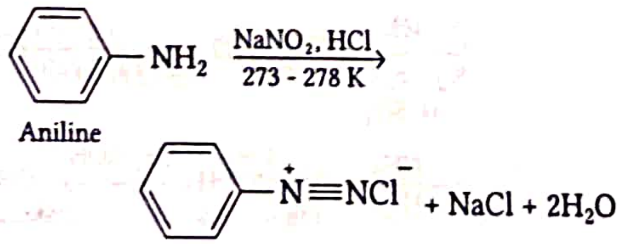
37. (i)



(ii) $CH_3-Cl \xrightarrow{KCN} \underset{(A)}{CH_3.CN} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3.CH_2NH_2}$

$\xrightarrow{CHCl_3+KOH\,(alc)} \underset{(C)}{CH_3.CH_2NC}$

38. (i) **Nitrous acid test** Aniline with HNO_2 (from $NaNO_2 + HCl$) gives benzene diazonium chloride which is stable at 273-278 K and hence, does not decompose to give N_2 gas.



Aniline

Benzene diazonium chloride

While benzylamine reacts with HNO_2, it give diazonium salt which being unstable at low temperature decomposes and gives N_2 gas.

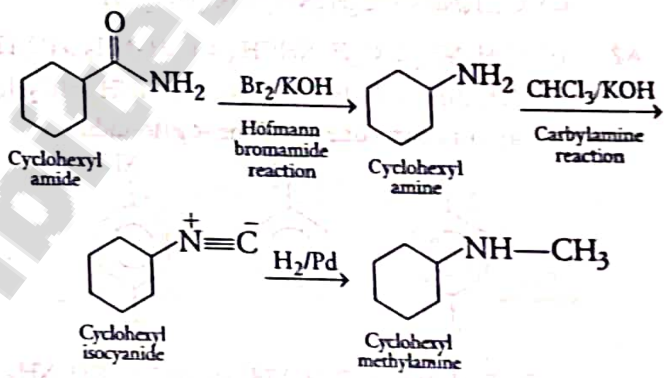
$$C_6H_5CH_2NH_2 \xrightarrow{NaNO_2/\,HCl} \underset{\text{(Unstable)}}{[C_6H_5CH_2-\overset{+}{N}\equiv NCl^-]}$$

$$\xrightarrow{H_2O} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + N_2\uparrow + HCl$$

(ii) Aniline is a primary aromatic amine while N-methyl aniline is a secondary aromatic amine. So, they can be distinguished by carbylamine test.

For test, refer to text on page 372.

39. Complete conversion can be performed as

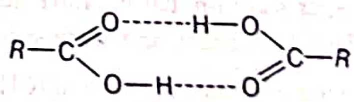


40. (i) The correct increasing order of solubility in water is aniline < 3 - ethyl ethanamine <ethanamine

Solubility of amines decreases with increase in molar mass due to increase in the hydrophobic part which retard the formation of H - bonds.

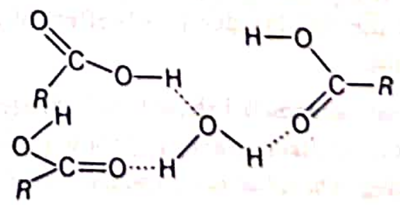
(ii) The correct increasing order of boiling point is ethanamine < ethanol < ethanoic acid.

Carboxylic acids have higher boiling points because they have high extent of hydrogen bonding with water, due to which they exists as associated molecules.



Dimer

In vapour state or in aprotic solvent



Hydrogen bonding of RCOOH with H_2O

(iii) The correct increasing order of basic strength in aqueous phase is

N, N - dimethylmethanamine < methanamine < N - methyl methanamine
(3°) (1°) (2°)

Basic strength in aqueous phase depends upon the stabilisation of their conjugate acids by a number of factors such as H - bonding, steric hindrance of alkyl groups and $+I$ efffect of alkyl groups. The first two factors are favourable for 2° amines.

41. (i) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

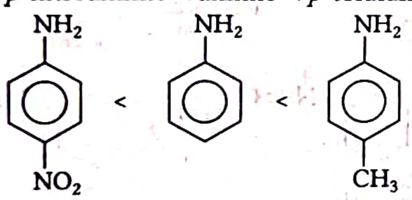
(ii) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

(iii) $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

42. (i) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2\ NH$

(ii) $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2\ NH$

(iii) (a) p-nitroaniline < aniline < p-toluidine



(b) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

43. (i) $C_2H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

(ii) $C_6H_5NH_2 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

(iii) $C_6\ H_5NH_2 < C_6\ H_5CH_2NH_2 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$

44. (i) Aniline being a Lewis base, react with the Lewis acid $AlCl_3$ used in Friedel-Crafts reaction and produce a salt, hence does not show Friedel-Crafts reaction.

$$C_6H_5 \cdot NH_2 + AlCl_3 \longrightarrow C_6H_5 \cdot \overset{+}{N}H_2 \cdot AlCl_3^- \text{ (Salt)}$$

(ii) In aqueous solution, basic nature depends on $+I$-effect, H-bonding and steric-effect.

The combined effect shows that $(CH_3)_2 \cdot NH$ is more basic than $(CH_3)_3 \cdot N$ as H-bonding is more in case of $(CH_3)_2 \cdot NH$ than in $(CH_3)_3N$, which predominates over the stability due to $+I$- effect of three — CH_3 groups.

(iii) Primary amines (1°) show two-hydrogen bonds whereas tertiary amines (3°) show no hydrogen bonding. Thus, the net attractive force in case of primary amines is more than that of tertiary amines. Hence, primary amines have higher boiling point than that of tertiary amines.

45. Four structural isomers are possible.

$CH_3—CH_2—CH_2—NH_2$,
Propan-1-amine
(1° amine)

$CH_3—NH—C_2H_5$,
N-methyl ethanamine
(2° amine)

$CH_3—\underset{NH_2}{\underset{|}{C}H}—CH_3$
Propan-2-amine
(1° amine)

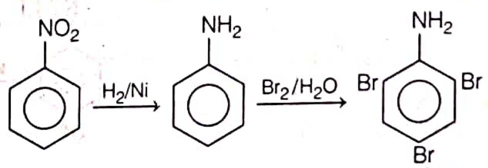
Only 1° amines react with HNO_2 to give N_2 gas, i.e.

$$\underset{\text{Propan-1-amine}}{CH_3—CH_2—CH_2—NH_2} + HONO \longrightarrow \underset{\text{Propan-1-ol (Major product)}}{CH_3—CH_2—CH_2OH} + N_2\uparrow + H_2O$$

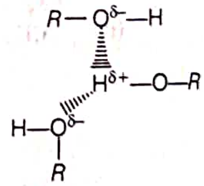
$$\underset{\text{Propan-2-amine}}{(H_3C)_2CH—NH_2} + HONO \longrightarrow \underset{\text{Propan-2-ol (Major product)}}{(H_3C)_2CH—OH} + N_2\uparrow + H_2O$$

46. (i) N - methylethanamine is secondary amine. When it reacts with benzene sulphonyl chloride it forms N-ethyl-N-methyl sulphonamide while, N, N - dimethylethanamine is a tertiary amine. It does not react with benzene sulphonyl chloride.

(ii)



(iii) Butan-1-ol is more soluble in water. Alcohol forms stronger hydrogen bonds with water than formed by amine due to higher electronegativity of O in alcohol than N in amine.



47. (i) Ethanamine into methanamine

$$\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\xrightarrow[K_2\,Cr_2\,O_7\,/H_2SO_4]{[O]} CH_3CHO \xrightarrow[K_2Cr_2O_7/H_2SO_4]{[O]} CH_3COOH$$

$$\xrightarrow[\text{Heat}]{NH_3} \underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(ii) Ethanoic acid into propanoic acid

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{Red\ P/I_2}$$

$$\underset{\text{Iodoethane}}{CH_3CH_2I} \xrightarrow{KCN(alc.)} \underset{\text{Propane nitrile}}{CH_3CH_2CN} \xrightarrow{H_2O/H^+} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

(iii) Methanamine into ethanamine

$$\underset{\text{Methanamine}}{CH_3NH_2} \xrightarrow[-N_2,\ -H_2O]{HONO} \underset{\text{Methanol}}{CH_3OH} \xrightarrow{Red\ P/I_2}$$

$$\underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{KCN(alc.)} \underset{\text{Ethane nitrile}}{CH_3CN} \xrightarrow[4[H]]{Na/C_2H_5OH/\ Reduction} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

48. (i) Ethanoic acid into methanamine

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{SOCl_2} \underset{\text{Ethanoyl chloride}}{CH_3COCl} \xrightarrow{NH_3(excess)}$$

$$\underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\text{Hofmann bromamide reaction}]{Br_2/\ KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(ii) Hexane nitrile into 1-aminopentane

$$\underset{\text{Hexane nitrile}}{CH_3(CH_2)_4CN} \xrightarrow[\text{Partial hydrolysis}]{H_3O^+} \underset{\text{Hexanamide}}{CH_3(CH_2)_4CONH_2}$$

$$\xrightarrow[\text{Hofmann bromamide reaction}]{Br_2/KOH} \underset{\text{1-aminopentane}}{CH_3(CH_2)_4NH_2}$$

(iii) Methanol into ethanoic acid

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{PCl_5} \underset{\text{Chloromethane}}{CH_3Cl} \xrightarrow{KCN(alc.)}$$

$$\underset{\text{Ethane nitrile}}{CH_3CN} \xrightarrow{H_3O^+} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

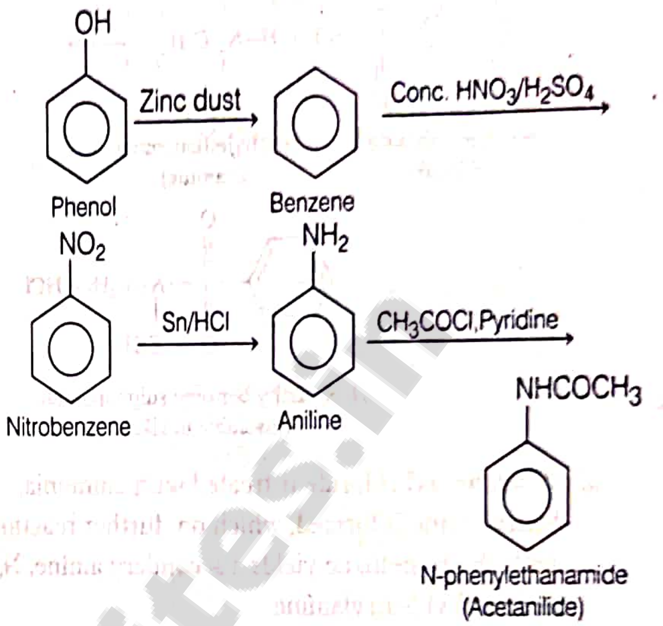
49. (i) $\underset{\text{Ethyl bromide}}{CH_3CH_2Br} \xrightarrow{KCN} \underset{\text{Ethyl cyanide (A)}}{CH_3CH_2CN} \xrightarrow{LiAlH_4}$

$$\underset{\substack{n\text{-propylamine}\\(B)}}{CH_3CH_2CH_2NH_2} \xrightarrow[0°C]{HNO_2} \underset{\substack{n\text{-propyl alcohol}\\(C)}}{CH_3CH_2CH_2OH}$$

(ii) $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[Heat]{NH_3} \underset{\substack{\text{Acetamide}\\(A)}}{CH_3CONH_2} \xrightarrow{NaOBr}$

$$\underset{\substack{\text{Methyl amine}\\(B)}}{CH_3NH_2} \xrightarrow{NaNO_2/HCl} \underset{\substack{\text{Methanol}\\(C)}}{CH_3OH}$$

50. (i) **Phenol to N-phenylethanamide**



(ii) **Chloroethane to methanamine**

$$\underset{\text{Chloroethane}}{CH_3CH_2Cl} \xrightarrow{Aq.\ NaOH} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{KMnO_4}$$

$$CH_3COOH \xrightarrow{NH_3/Heat} CH_3CONH_2 \xrightarrow{Br_2/KOH}$$

$$CH_3NH_2$$

(iii) **Propane nitrile to ethanal**

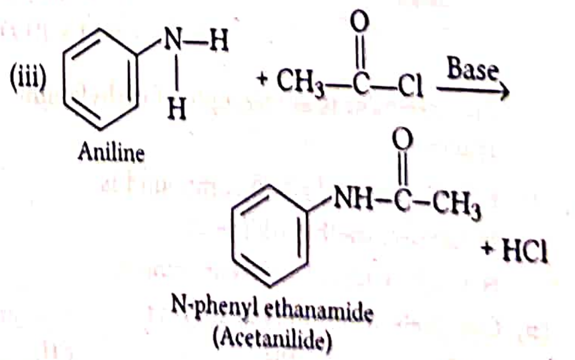
$$\underset{\text{Propane nitrile}}{CH_3CH_2CN} \xrightarrow{H_3O^+} \underset{\text{Propanamide}}{CH_3CH_2CONH_2} \xrightarrow{Br_2/NaOH}$$

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{PCC} \underset{\text{Ethanal}}{CH_3CHO}$$

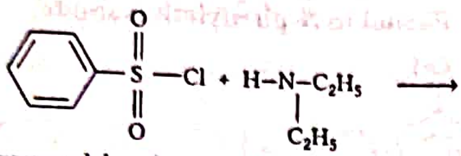
51. (i) $\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + HNO_2 \xrightarrow{0°C} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + N_2\uparrow + H_2O$

(ii) Refer to text on page 373.

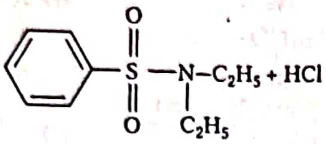
(iii)



52. (i) When N-ethylethanamine (2°amine) reacts with benzenesulphonyl chloride N, N-diethylbenzene sulphonamide is formed.

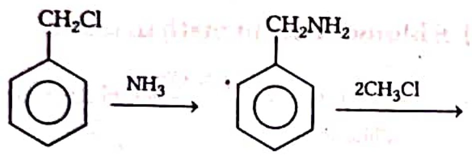


Benzene sulphonyl chloride　　N-ethylethanamine (2° amine)

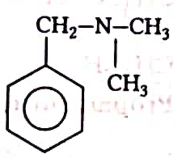


N, N-diethylbenzene sulphonamide
(Insoluble in alkali)

(ii) When benzyl chloride is treated with ammonia, benzylamine is formed, which on further reaction with chloromethane yields a secondary amine, N, N-dimethyl benzylamine.

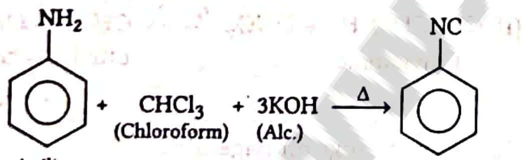


Benzyl chloride　　Benzylamine



N-N-dimethylbenzylamine
(2° amine)

(iii) Aniline on reaction with chloroform in the presence of alcoholic potassium hydroxide gives phenyl isocyanides (or phenyl isonitrile).

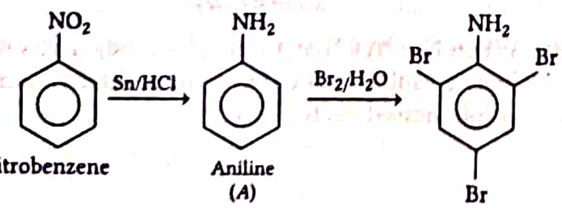


Aniline　　Phenyl isocyanide
$+ 3KCl + 3H_2O$

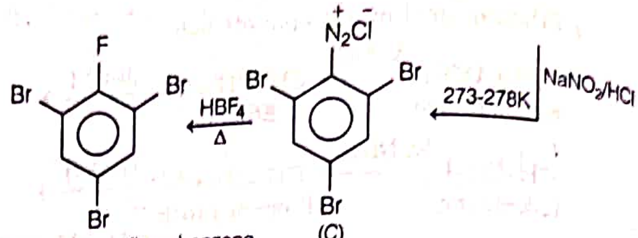
This reaction is an example of carbylamine reaction.

53. (i) IUPAC name of given compound is N-ethyl-N-methylaniline or N-ethyl-N-methylbenzenenamine.

(ii) Complete reaction is as follows



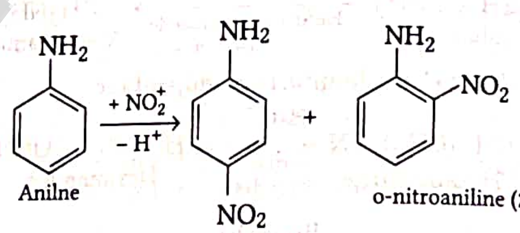
Nitrobenzene　　Aniline (*A*)　　2,4,6-tribromoaniline (*B*)



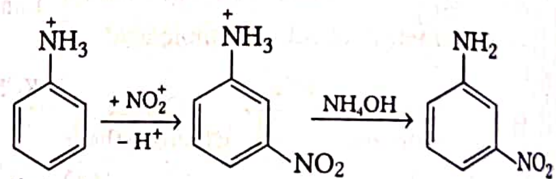
2,4,6-tribromofluorobenzene (*D*)　　(*C*)

54. (i) Nitration is usually carried out with a mixture of conc. HNO_3 and conc. H_2SO_4. So, in the presence of these acids, aniline gets protonated to form anilinium ion. Therefore, in the presence of these acids, the reaction mixture consists of aniline and anilinium ion. —NH_2 group in aniline is o, *p*-directing and activating, whereas the $\overset{+}{N}H_3$ group in anilinium ion is *m*-directing and deactivating.

Now, nitration of aniline mainly gives *p*-nitroaniline due to steric hindrance at *o*-position, the nitration of anilinium ion gives *m*-nitroaniline. In actual practice approx. 1 : 1 mixture of *p*-nitroaniline and *m*-nitroaniline is obtained.



Anilne　　o-nitroaniline (2%)
p-nitroaniline (51%)



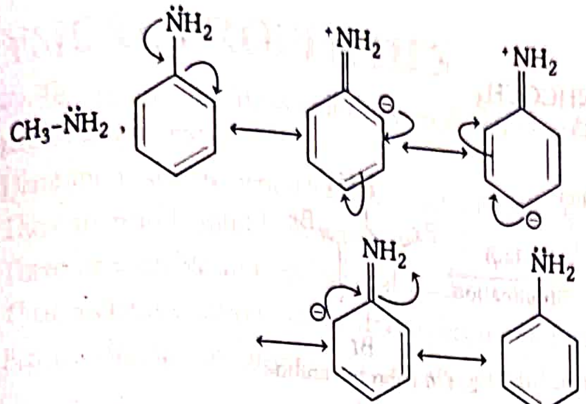
Anilinium ion　　m-nitroaniline (47%)

(ii) Gabriel phthalimide synthesis produces primary amines only without the traces of secondary or tertiary amines. So, this method is preferred for the synthesis of primary amines.

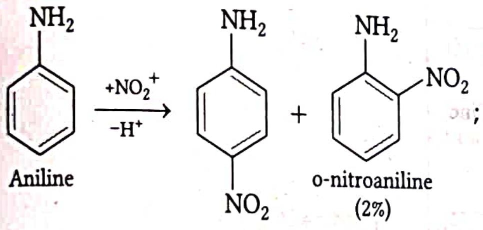
For reactions, refer to text on page 363.

55. (i) Due to electron withdrawing effect of the acetyl group, the lone pair of electrons on N-atom is attracted by group.As a result, lone pair of electrons on N-atom is not exclusively available for donation to the benzene ring and hence, activating effect of the — NH_2 group is reduced.

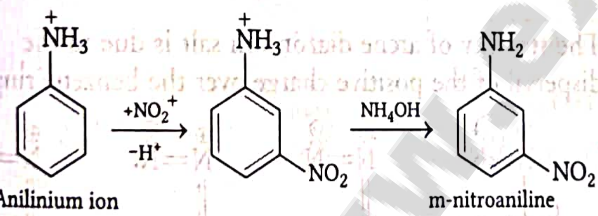
(ii) In aniline ($C_6H_5NH_2$), the electron pair on nitrogen atom is involved in conjugation with ring and is less available for protonation than that in methylamine (CH_3NH_2). Therefore, aniline is less basic than methylamine.



(iii) Nitration is usually carried out with a mixture of conc. HNO_3 and conc. H_2SO_4. So in the presence of these acids, aniline gets protonated to form anilinium ion. Therefore, the reaction mixture consists of aniline and anilinium ion. $-NH_2$ group in aniline is o, p-directing and activating, whereas the NH_3 group in anilinium is m -directing and deactivating. Now, nitration of aniline mainly gives p-nitroaniline due to steric hindrance at o-position and the nitration of anilinium ion gives m -nitroaniline.



Aniline; p-nitroaniline (51%); o-nitroaniline (2%)



Anilinium ion; m-nitroaniline (47%)

56. (i) The C—Cl bond of chlorobenzene has partial double bond (due to resonance or +M-effect). Thus, it is very difficult to break it. So, under normal condition ammonia is unable to displace chlorine from chlorobenzene and aniline is not formed.

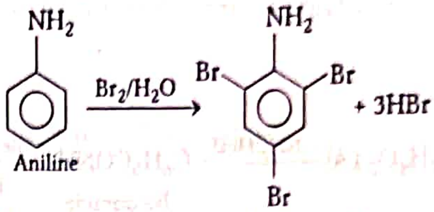
(ii) Amines are polar and hence form intermolecular H-bonds. This intermolecular association depends upon the extent of H-bonding. 1° amines have two, 2° amines have one, while 3° amines have no hydrogen bonded to nitrogen. Therefore, boiling point of butanamine is higher than N-ethylethanamine.

$CH_3CH_2CH_2CH_2NH_2$ Butanamine (1° amine)

$CH_3CH_2-\underset{H}{\underset{|}{N}}-CH_2CH_3$ N-ethylethanamine (2° amine)

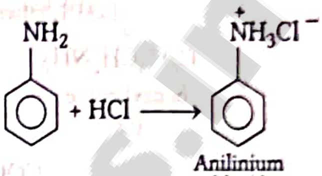
(iii) Acylation of aniline is carried out in the presence of a base stronger than amine like pyridine, which remove HCl so formed and shifts the equilibrium towards right hand side.

57. (i) (a)



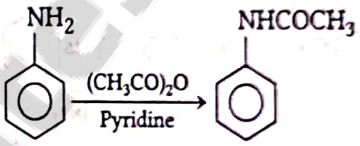
Aniline; 2, 4, 6-tribromoaniline

(b)



Anilinium chloride

(c)



Acetanilide

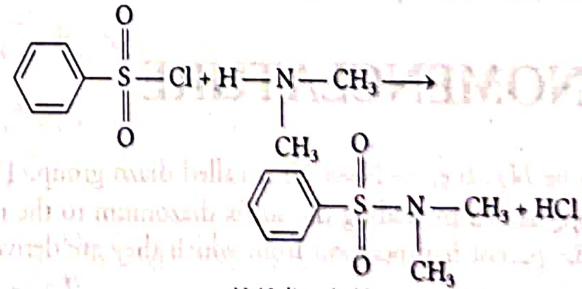
(ii) Alcohols have higher boiling point as compared to that of amines, because oxygen being more electronegative atom, forms strong hydrogen bond as compared to that of nitrogen.

In tertiary amine, there is no hydrogen bond formation due to the absence of H-atoms and hence, has the lowest boiling point.

Therefore, increasing order of boiling point

$(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$

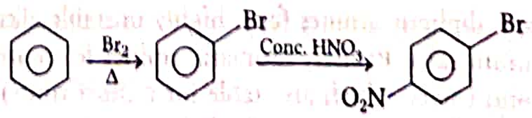
(iii) $(CH_3)_2NH$ and $(CH_3)_3N$ are secondary and tertiary amines respectively. These are distinguished by Hinsberg's reagent which gives sulphonamide with secondary amines and no reaction carried out with tertiary amines. $(CH_3)_2NH$ reacts with benzene sulphonyl chloride as follows:



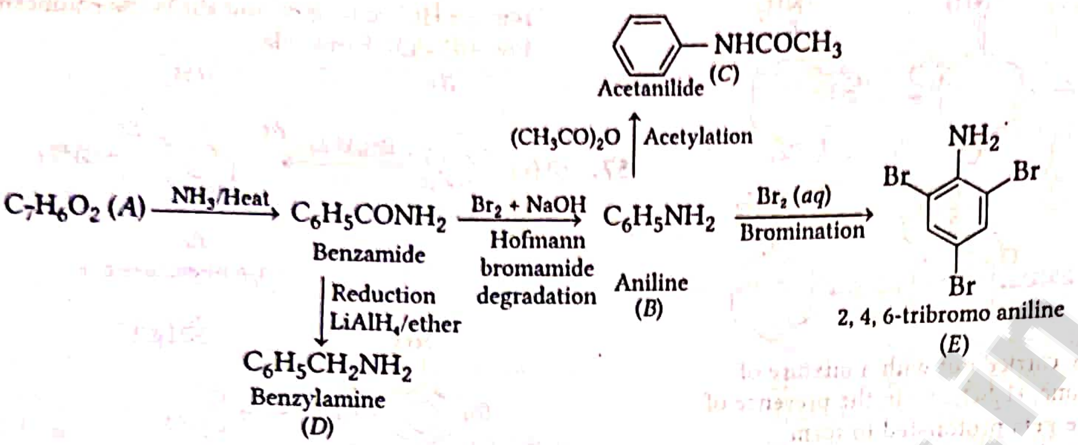
N, N-dimethyl benzene sulphonamide

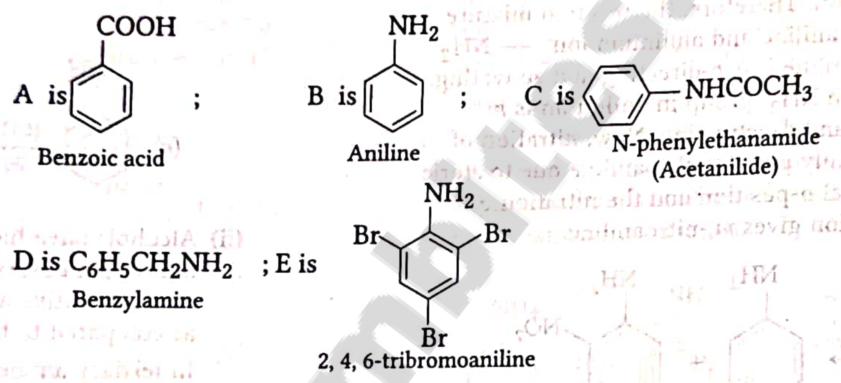
58. (i) Refer to text on page 373.

(ii) Hint $A = C_2H_5-\underset{H}{\underset{|}{N}}-CH_3$



59.





|TOPIC 3|

Diazonium Salts

Diazonium salts are a group of organic compounds, having the general formula, $Ar\overset{+}{N_2}\bar{X}$, where Ar is abbreviated for the aryl group and $\bar{X}$ may be $Cl^-, Br^-, HSO_4^-, NO_3^-$, etc.

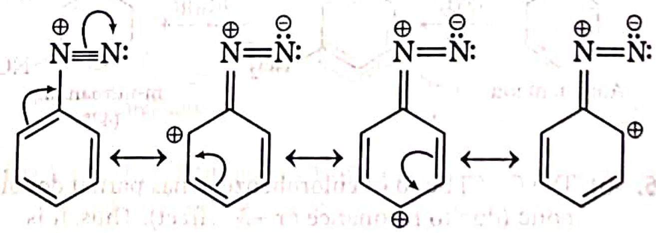
NOMENCLATURE

The $\overset{+}{N_2}$, (i.e. $-\overset{+}{N}\equiv N$) is called diazo group. These are named by adding the suffix diazonium to the name of the parent hydrocarbon from which they are derived followed by the name of anion. e.g. $C_6H_5\overset{+}{N_2}\bar{Cl}$ is benzene diazonium chloride, $C_6H_5N_2^+HSO_4^-$ is benzene diazonium hydrogen sulphate.

STABILITY

Primary aliphatic amines form highly unstable alkyl diazonium salts. Primary aromatic amines form arene diazonium salts, which are stable for a short time in solution at low temperature (0-5°C).

The stability of arene diazonium salt is due to the dispersal of the positive charge over the benzene ring.



Note Resonance stabilisation is not possible in diazonium salts of aliphatic amines.

METHOD OF PREPARATION

Benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid (which is produced by the reaction of $NaNO_2$ and HCl) at 273-278 K or 0-5°C.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278\ K} C_6H_5\overset{+}{N_2}\bar{Cl} + NaCl + 2H_2O$$

The conversion of primary aromatic amines into their diazonium salts is called **diazotisation.** Due to its instability, the diazonium salt is not generally stored and is used immediately after its preparation.

PHYSICAL PROPERTIES

Benzene diazonium chloride is colourless and readily soluble in water. Hence, physical properties of diazonium salts can be described as follows:

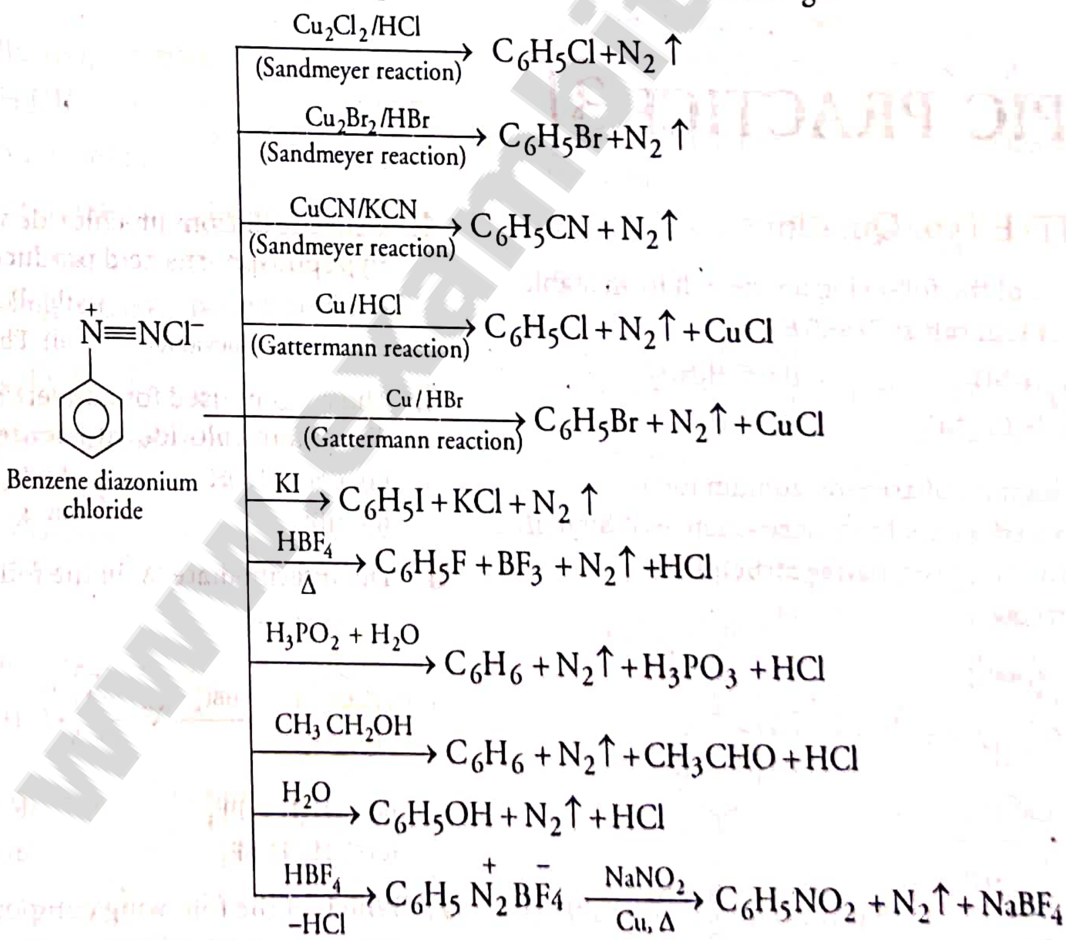
(i) Diazonium salts are generally colourless, crystalline solids.
(ii) These are readily soluble in water and stable in cold water. They react with water when warmed.
(iii) These are unstable and exploit in dry state, hence used in solution state.
(iv) Their aqueous solutions are neutral to litmus and conduct electricity due to the presence of ions.
(v) Benzene diazonium fluoroborate is water insoluble and stable at room temperature.

CHEMICAL REACTIONS

The chemical reactions of diazonium salts can be divided into two categories:

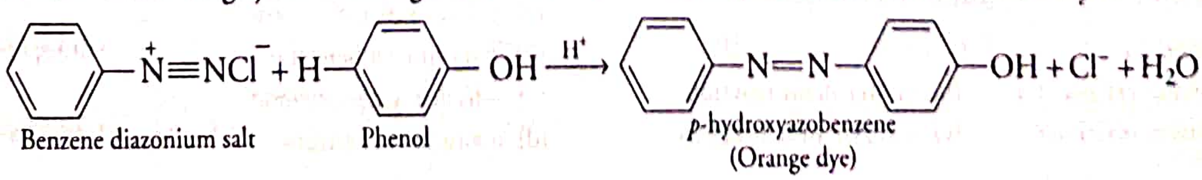
Reactions Involving Displacement of Nitrogen

Diazonium group being a very good leaving group, is substituted by other groups such as Cl^-, Br^-, I^-, CN^- and OH^- from the aromatic ring. The nitrogen thus formed escapes from the reaction mixture as a gas.

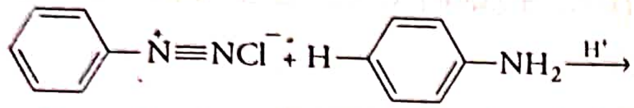


Reactions Involving Retention of Diazo Group (Coupling Reactions)

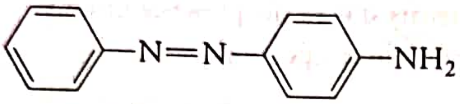
Benzene diazonium chloride reacts with phenol in which phenol molecule at its *para*-position is coupled with diazonium salt to give the product *p*-hydroxy azobenzene, hence the reaction is known as coupling reaction. The azo products obtained having both the aromatic rings joined through the —N=N— bonds, are coloured and used as dyes.



Similarly, the reaction of diazonium salt with aniline gives *p*-aminoazobenzene (yellow dye).



Benzene diazonium salt   Aniline



p-aminoazobenzene
(Yellow dye)

$+ Cl^- + H_2O$

IMPORTANCE OF DIAZONIUM SALTS IN THE SYNTHESIS OF AROMATIC COMPOUNDS

These are important in the synthesis of aromatic compounds due to the following facts:

(i) These are very good intermediates for the introduction of —F, —Cl, —OH, —CN, —NO_2, etc., into the aromatic ring.

(ii) Similarly, aryl fluorides and iodides cannot be prepared by the direct halogenation. Cyano group cannot be introduced by nucleophilic substitution reaction but cyanobenzene can be prepared from diazonium salts.

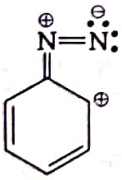
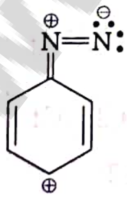
(iii) Thus, replacement of diazo group by the other group is helpful in preparing those aromatic compounds which cannot be prepared by the direct substitution in benzene.

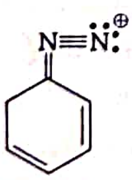
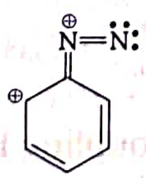
TOPIC PRACTICE 3

OBJECTIVE Type Questions

1. Which of the following amine will form stable diazonium salt at 273-278 K?
(a) $C_2H_5NH_2$ (b) $C_6H_5NH_2$
(c) $C_6H_5CH_2NH_2$ (d) $C_6H_5N(CH_3)_2$

2. The stability of arenediazonium ion is explained on the basis of resonance. Which of the following resonating structure is incorrect?

(a)  (b) 

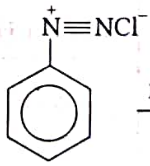
(c)  (d) 

3. The reaction,
$$ArN_2^+Cl^- \xrightarrow{Cu/HCl} ArCl + N_2 + CuCl$$
is named as
(a) Sandmeyer reaction (b) Gattermann reaction
(c) Claisen reaction (d) Carbylamine reaction

4. Benzene diazonium chloride when reacts with hypophosphorus acid produces
(a) Benzene (b) Phenol
(c) Phenol isocyanide (d) Phenyl phosphate

5. The reagent used for converting benzene diazonium chloride into benzene is
(a) CH_3CH_2OH (b) H_2O
(c) HBF_4 (d) KI

6. The intermediate '*X*' in the following reaction is

 $\xrightarrow{HBF_4}$ 'X' $\xrightarrow[Cu,\,\Delta]{NaNO_2}$ $C_6H_5NO_2 + N_2\uparrow + NaBF_4$

(a) $C_6H_5N=BF_4$ (b) $C_6H_5\overset{+}{N_2}\,\overset{-}{BF_4}$
(c) $C_6H_5N_2^+\,BF_2^-$ (d) $C_6H_5N{=}NBF_4$

7. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride? **NCERT Exemplar**
(a) Aniline (b) Phenol
(c) Anisole (d) Nitrobenzene

8. The correct name for yellow dye is
(a) *p*-hydroxy azobenzene
(b) *p*-amino azobenzene
(c) *o*-hydroxy azobenzene
(d) *o*-amino azobenzene

VERY SHORT ANSWER Type Questions

9. What is a diazo group?

10. Diazonium salts of aromatic amines are more stable than those of aliphatic amines. Explain. **NCERT**

11. Benzene diazonium salts are more stable than alkyl diazonium salts. Give reason.

12. Write a short note on diazotisation. **NCERT**

13. The conversion of primary aromatic amines into diazonium salts is known as **Delhi 2014**

14. Benzene diazonium chloride is not stored and used immediately after its preparation. Give reason.

15. Why diazonium group gets easily substituted by other groups?

16. Complete the following reaction.

$C_6H_5N_2Cl + C_2H_5OH \longrightarrow$ **NCERT**

17. Define Gattermann reaction.

18. Write a short note on coupling reaction.

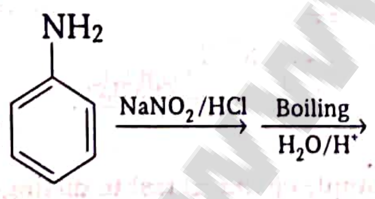
Or

Explain the coupling reaction. **Delhi 2013 C; NCERT**

SHORT ANSWER Type I Questions

19. Complete the following reactions.

(i) $C_6H_5N_2^+Cl^- \xrightarrow[\text{(Room temperature)}]{H_2O}$

(ii) 

All India 2013

20. Complete the following reactions.

(i) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(ii) $C_6H_5N_2Cl \xrightarrow[\text{(ii) } NaNO_2/Cu]{\text{(i) } HBF_4}$

All India 2013, 2012; NCERT

SHORT ANSWER Type II Questions

21. Identify *A*, *B* and *C* in the following reactions:

(i) $CH_3CH_2Cl \xrightarrow{KCN} A \xrightarrow{H_2/Ni} B \xrightarrow{CH_3COCl/Base} C$ **All India 2017 C**

(ii) $C_6H_5N_2^+ Cl^- \xrightarrow{HBF_4} A \xrightarrow[\Delta]{NaNO_2/Cu} B \xrightarrow{Sn/HCl} C$

22. Accomplish the following conversions.

(i) Aniline to 2, 4, 6-tribromofluorobenzene

(ii) Nitrobenzene to benzoic acid

(iii) Benzene to *m*-bromophenol **Delhi 2012; NCERT**

23. Accomplish the following conversions.

(i) Aniline to *p*-bromoaniline

(ii) Benzamide to toluene

(iii) Aniline to benzyl alcohol **Delhi 2012; NCERT**

24. Give the structures of *A*, *B* and *C* in the following reactions.

(i) $C_6H_5\overset{+}{N_2}Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/\ H^+} B \xrightarrow[\Delta]{NH_3} C$

(ii) $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

NCERT; Delhi 2014, 2013

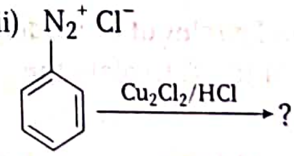
25. Convert

(i) 3-methyl aniline into 3-nitrotoluene.

(ii) aniline into 1, 3, 5-tribromobenzene. **NCERT Intext**

26. Write the major product(s) in the following reactions.

(i) $C_6H_5-NO_2 \xrightarrow{Sn/HCl} ?$

(ii) 

All India 2016

(iii) $CH_3CONH_2 \xrightarrow{Br_2/KOH(aq.)} ?$ **Delhi 2016 C**

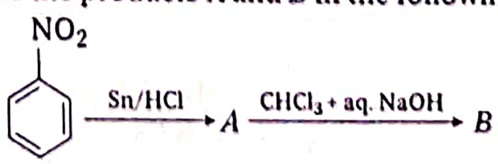
27. Write the structures of compounds *A*, *B* and *C* in the following reactions.

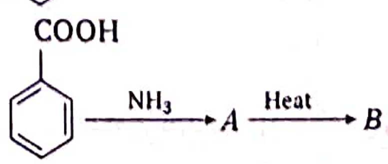
(i) $CH_3-COOH \xrightarrow{NH_3/\Delta} A \xrightarrow{Br_2/KOH(aq)} B \xrightarrow{CHCl_3 + alc.\ KOH} C$

(ii) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Fe/HCl} B \xrightarrow{CH_3COCl/pyridine} C$

All India 2017

28. Write the products *A* and *B* in the following.

(i) 

(ii) 

(iii) $C_6H_5\overset{+}{N_2}Cl^- \xrightarrow{Cu/HCl} A \xrightarrow{Cl_2/FeCl_3} B$

All India 2016 C

29. Give the structures of A, B and C in the following reactions.

(i) $C_6H_5NO_2 \xrightarrow{Fe / HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O / H^+} C$

(ii) $C_6H_5NO_2 \xrightarrow{Fe / HCl} A \xrightarrow[273\ K]{HNO_2} B \xrightarrow{C_6H_5OH} C$ **NCERT**

30. Give one chemical test to distinguish between the following pairs of compounds.

(i) Methylamine and dimethylamine
(ii) Secondary and tertiary amines
(iii) Ethylamine and aniline

NCERT; All India 2012, 2011

LONG ANSWER Type Questions

31. A hydrocarbon 'A' (C_4H_8) on reaction with HCl gives a compound 'B' (C_4H_9Cl), which on reaction with 1 mole of NH_3 gives compound 'C' ($C_4H_{11}N$). On reacting with $NaNO_2$ and HCl followed by the treatment with water, compound 'C' yields an optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 moles of acetaldehyde. Identify compounds 'A' to 'D'. Explain the reactions involved.

32. An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below.

Write the structures of A, B, C, D and E in the following reactions.

$$\underset{A}{(C_7H_7ON)} \xrightarrow{Br_2 + KOH} C_6H_5NH_2 \xrightarrow{CHCl_3 + NaOH} D$$

$$C_6H_5NH_2 \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow{CH_3CH_2OH} C$$

$$B \xrightarrow{KI} E$$

Delhi 2015

33. (i) Write the structures of main products when benzene diazonium chloride reacts with the following reagents :

(a) $H_3PO_2 + H_2O$ (b) $CuCN / KCN$ (c) H_2O

(ii) Arrange the following in the increasing order of their basic character in an aqueous solution :

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$

(iii) Give a simple chemical test to distinguish between the following pair of compounds:

$C_6H_5—NH_2$ and $C_6H_5—NH—CH_3$

All India 2015

34. (a) Write the reactions involved in the following:

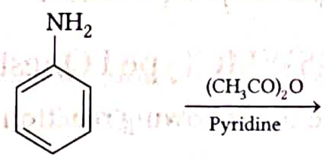
(i) Hofmann bromamide degradation reaction
(ii) Diazotisation **CBSE 2018**
(iii) Gabriel phthalimide synthesis

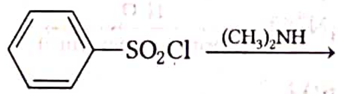
(b) Give reasons:

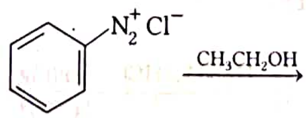
(i) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.
(ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts.

Or

(a) Write the structures of the main products of the following reactions:

(a) 

(b) 

(c) 

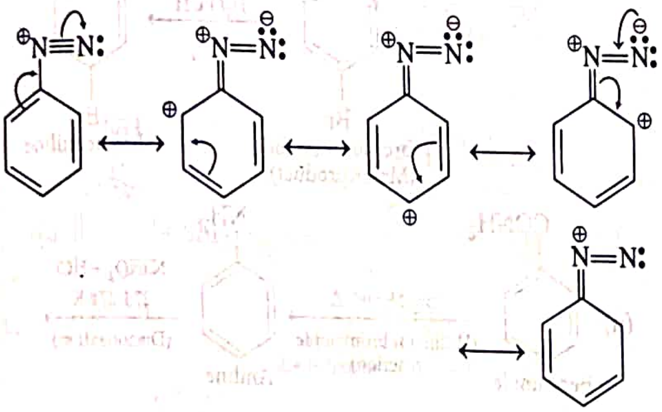
(b) Give a simple chemical test to distinguish between aniline and N, N-dimethylaniline.

(c) Arrange the following in the increasing order of their pK_b values: $C_6H_5NH_2$, $C_2H_5NH_2$, $C_6H_5NHCH_3$

HINTS AND EXPLANATIONS

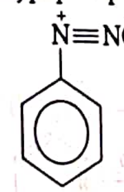
1. (b) Primary aromatic amines form arene diazonium salts which are stable for a short time in solution at low temperatures (273-278 K).

2. (c) The stability of arenediazonium ion is explained on the basis of resonance as below.



3. (b) Chlorine or bromine can be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as Gattermann reaction.

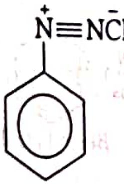
4. (a) Benzene diazonium chloride when reacts with hypophosphorus acid produces benzene.



Benzene diazonium salt

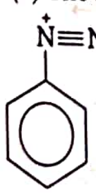
$$\xrightarrow{H_3PO_2+H_2O} \underset{\text{Benzene}}{C_6H_6} + N_2\uparrow + H_3PO_3 + HCl$$

5. (a) CH_3CH_2OH can be used for converting benzene diazonium chloride into benzene



$$\xrightarrow{CH_3CH_2OH} C_6H_6 + N_2\uparrow + CH_3CHO + HCl$$

6. (b) The intermediate 'X' is $C_6H_5\overset{+}{N_2}\overset{-}{B}F_4$



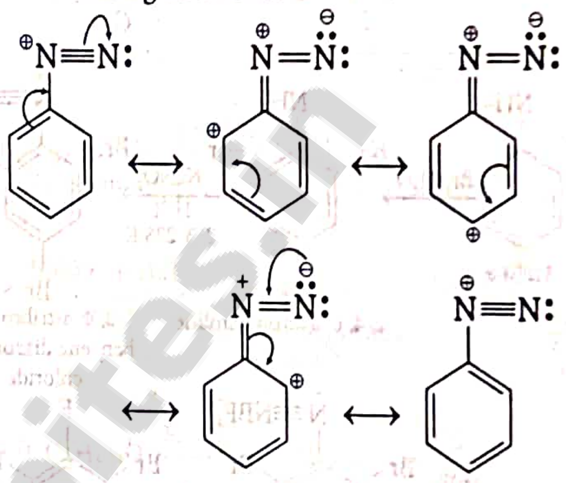
$$\xrightarrow[-HCl]{HBF_4} C_6H_5\overset{+}{N_2}BF_4^- \xrightarrow[Cu,\,\Delta]{NaNO_2} C_6H_5NO_2 + N_2\uparrow + NaBF_4$$

7. (d) Nitrobenzene will not undergo azo coupling reaction with benzene diazonium chloride while other three undergo diazo coupling reaction very easily. Diazonium cation is a weak E^+ and hence reacts with electron rich compounds containing electron donating groups i.e. —OH, —NH_2 and —OCH_3 groups and not with compounds containing electron withdrawing group, i.e. NO_2 etc.

8. (b) The correct name for yellow dye is *p*-amino azobenzene. It is formed by the reaction between diazonium salt and aniline.

9. $\overset{+}{N}_2(\text{—}\overset{+}{N}\equiv N)$

10. Diazonium salts of aromatic amines are more stable than those of aliphatic amines due to the delocalisation of the positive charge on the benzene ring as shown below by the resonating structures.



11. Due to the dispersal of positive charge over benzene ring.

12. The conversion of primary aromatic amines into their diazonium salts is called diazotisation.

13. The conversion of primary aromatic amines into diazonium salts is known as diazotisation.

14. Benzene diazonium chloride is unstable or stable for a very short time in a solution at low temperature. Due to its unstability, it is used immediately after its preparation.

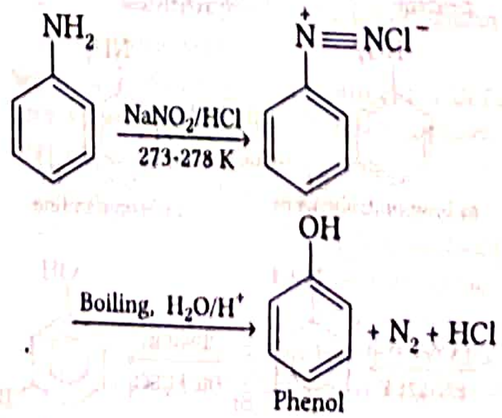
15. Because it is good leaving group.

16. $C_6H_5N_2Cl + C_2H_5OH \longrightarrow C_6H_6 + CH_3CHO + N_2\uparrow + HCl$

17. $C_6H_5N_2^+Cl^- \xrightarrow{Cu/HCl} C_6H_5Cl + N_2\uparrow\ CuCl$

18. Coupling reaction is the reaction of benzene diazonium chloride with phenol in which phenol molecule at its *para*-position is coupled with diazonium salt.

19. (i) $C_6H_5N_2^+Cl \xrightarrow[\text{Room temperature}]{H_2O} \underset{\text{Phenol}}{C_6H_5OH} + N_2\uparrow + HCl$

(ii) 

20. Refer to text on page 387.

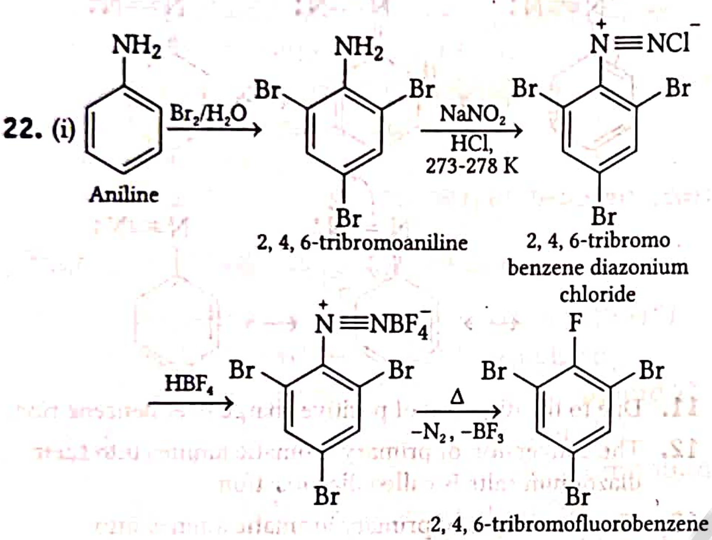
21. (i) $CH_3CH_2Cl \xrightarrow{KCN} \underset{A}{CH_3CH_2CN} \xrightarrow{H_2/Ni}$

$\underset{B}{CH_3CH_2NH_2} \xrightarrow{CH_3COCl/Base} \underset{C}{CH_3CH_2NHCOCH_3}$

(ii) $C_6H_5N_2^+Cl^- \xrightarrow{HBF_4} \underset{A}{C_6H_5N_2^+BF_4^-} \xrightarrow[\Delta]{NaNO_2/Cu}$

$\underset{B}{C_6H_5NO_2} \xrightarrow{Sn/HCl} \underset{C}{C_6H_5NH_2}$

22. (i)



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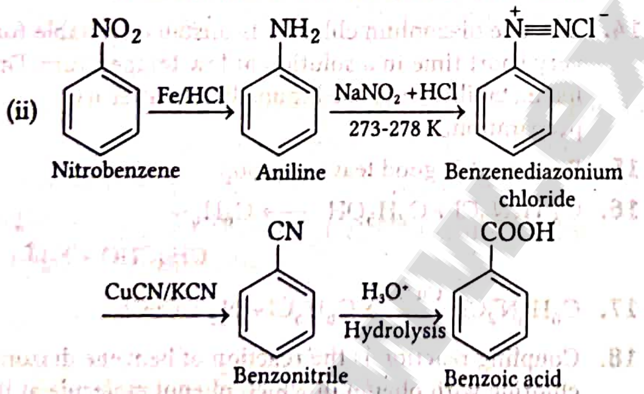

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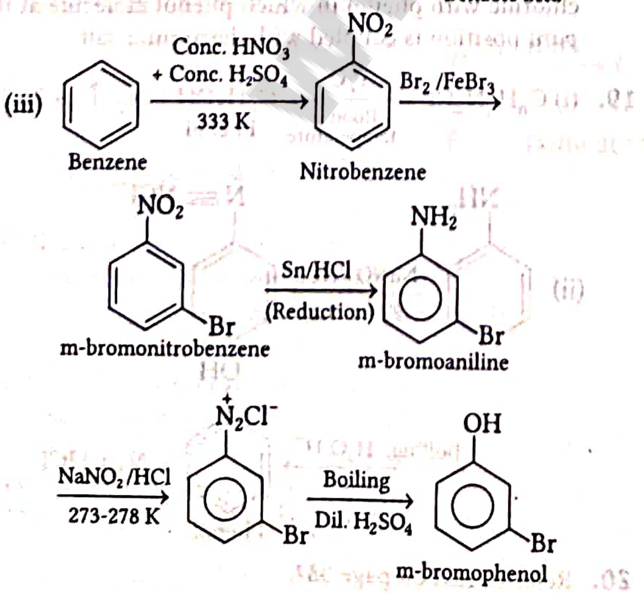
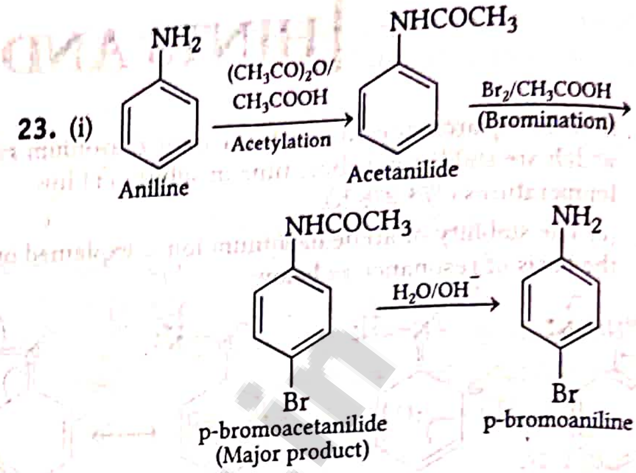
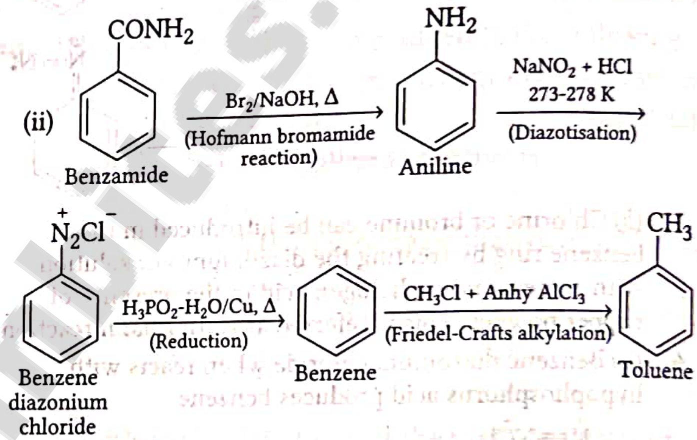


23. (i)



(ii)



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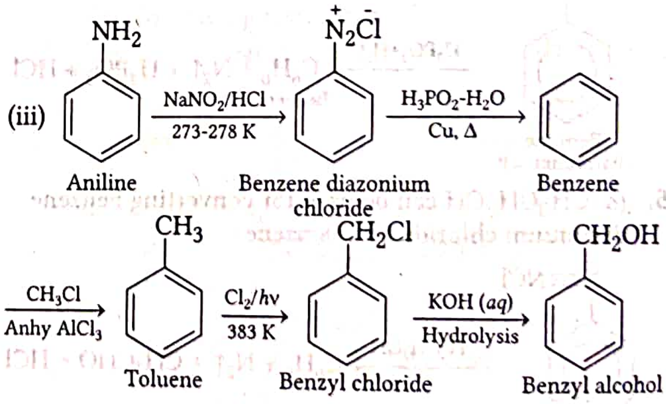
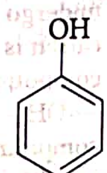


24. (i) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} \underset{\substack{\text{Benzonitrile}\\(A)}}{C_6H_5CN} \xrightarrow{H_2O/H^+}$

$\underset{\substack{\text{Benzoic acid}\\(B)}}{C_6H_5COOH} \xrightarrow[\Delta]{NH_3} \underset{\substack{\text{Benzamide}\\(C)}}{C_6H_5CONH_2}$

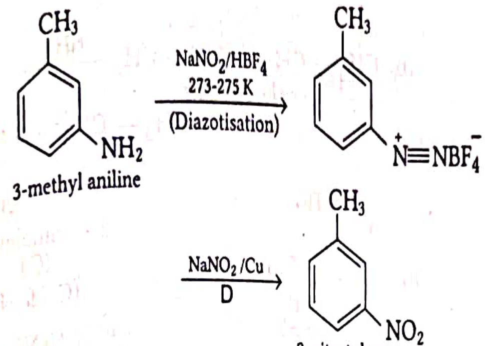
(ii) $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Sn+HCl} \underset{\substack{\text{Aniline}\\(A)}}{C_6H_5NH_2}$

$\xrightarrow[273\text{ K}]{NaNO_2 + HCl} \underset{\substack{\text{Benzene diazonium chloride}\\(B)}}{C_6H_5N_2^+Cl^-} \xrightarrow[\Delta]{H_2O/H^+}$



Phenol
(C)

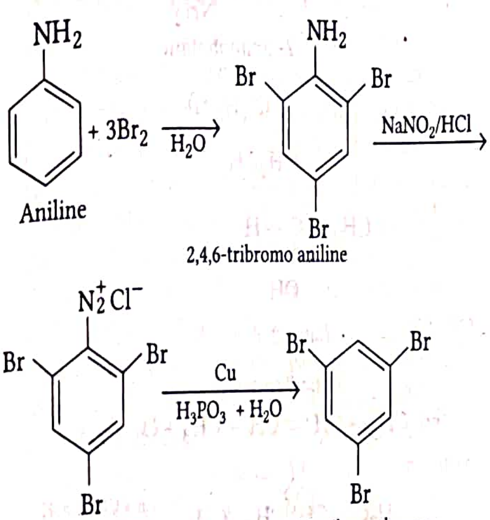
25\. (i)



3-methyl aniline

3-nitrotoluene

(ii)



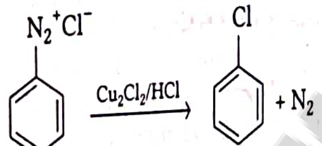
Aniline

2,4,6-tribromo aniline

1,3,5-tribromobenzene

26\. (i) $C_6H_5-NO_2 \xrightarrow{Sn/HCl} \underset{\text{Aniline}}{C_6H_5\cdot NH_2}$

(ii)



Chlorobenzene

(iii) $CH_3CONH_2 \xrightarrow{Br_2/KOH(aq)} CH_3NH_2 + K_2CO_3 + 2KBr + 2H_2O$

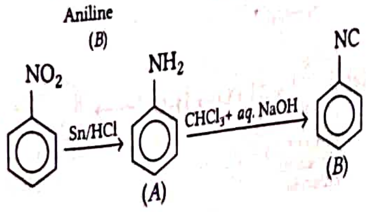
27\. (i) $\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-H_2O]{NH_3/\Delta} \underset{\text{Acetamide }(A)}{CH_3CONH_2} \xrightarrow{Br_2/KOH(aq)}$

$\underset{\substack{\text{Methylamine}\\(B)}}{CH_3NH_2} \xrightarrow{CHCl_3 + \text{alc. KOH}} \underset{\substack{\text{Methyl isocyanide}\\(C)}}{CH_3NC}$

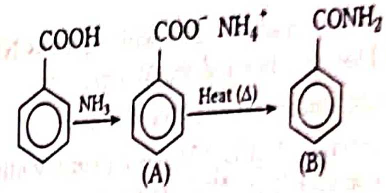
(ii) $C_6H_5\overset{+}{N_2}BF_4^- \xrightarrow[-N_2,-NaBF_4]{NaNO_2/Cu,\Delta} \underset{\substack{\text{Nitrobenzene}\\(A)}}{C_6H_5NO_2} \xrightarrow[\text{Reduction}]{Fe/HCl}$

$\underset{\substack{\text{Aniline}\\(B)}}{C_6H_5NH_2} \xrightarrow[-HCl]{CH_3COCl/\text{pyridine}} \underset{\substack{\text{Acetanilide}\\(C)}}{C_6H_5NHCOCH_3}$

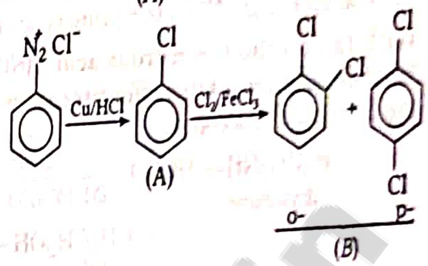
28\. (i)



(ii)



(iii)

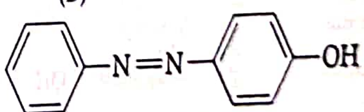


29\. (i) $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Fe/HCl} \underset{\substack{\text{Aniline}\\(A)}}{C_6H_5NH_2}$

$\xrightarrow[273\text{ K}]{NaNO_2 + HCl} \underset{\substack{\text{Benzene diazonium}\\\text{chloride}\\(B)}}{C_6H_5\overset{+}{N}\equiv NCl^-} \xrightarrow[\Delta]{H_2O/H^+} \underset{\substack{\text{Phenol}\\(C)}}{C_6H_5OH}$

(ii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} \underset{\substack{\text{Aniline}\\(A)}}{C_6H_5NH_2} \xrightarrow[273\text{ K}]{HNO_2}$

$\underset{\substack{\text{Benzene diazonium chloride}\\(B)}}{C_6H_5-\overset{+}{N}\equiv NCl^-} \xrightarrow[\text{Coupling reaction}]{C_6H_5OH}$



p-hydroxy azobenzene
(C)

30\. (i) **Carbylamine test** Methylamine is a primary amine, therefore it gives carbylamine test. When heated with an alcoholic solution of KOH and $CHCl_3$, it gives offensive smell of methyl isocyanide. Since, dimethylamine is a secondary amine hence, it does not give this test.

For reaction, refer to text on page 372.

$\underset{\substack{\text{Dimethylamine}\\(2^\circ\text{ amine})}}{(CH_3)_2NH} \xrightarrow[\Delta]{CHCl_3/KOH(alc.)} \text{No reaction}$

(ii) They can be distinguished by **Liebermann nitrosoamine test.**

Secondary (2°) amines on treatment with HNO_2, give yellow coloured oily N-nitrosoamines.

$\underset{\substack{\text{Diethylamine}\\(2^\circ\text{amine})}}{(CH_3CH_2)_2NH} + \underset{\text{Nitrous acid}}{HO-N=O} \longrightarrow$

$\underset{\substack{\text{N-nitrosodiethylamine}\\(\text{Yellow colour})}}{(CH_3CH_2)_2N-N=O} + H_2O$

N-nitrosodiethylamine, on warming with a crystal of phenol and conc. H_2SO_4, gives a green solution

which when made alkaline with aqueous NaOH turns deep blue and then red on dilution.

Tertiary amines do not give this test.

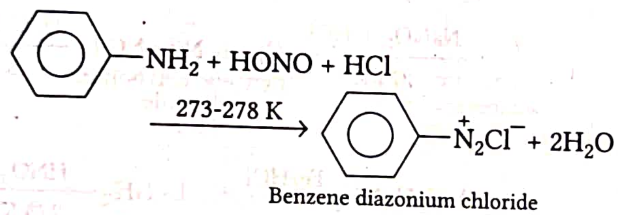
(iii) Ethylamine ($CH_3CH_2NH_2$) is a primary aliphatic amine while aniline ($C_6H_5NH_2$) is a primary aromatic amine.

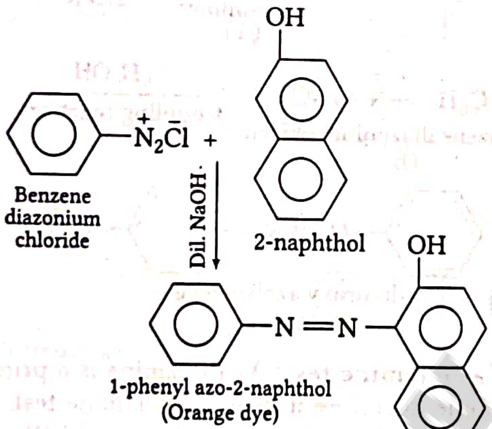
With the reaction of nitrous acid (HNO_2)

Ethylamine gives a brisk effervescence of N_2 gas with the formation of alcohol.

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + HONO \xrightarrow[\text{Dil. HCl(273-278 K)}]{NaNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH} + N_2\uparrow + H_2O$$

Whereas, aniline gives benzene diazonium chloride which on treatment with alkaline solution of β-naphthol (2-naphthol) gives an orange dye (azo dye test).





31. (i) Addition of HCl to compound '*A*' shows that compound '*A*' is alkene because compound '*B*' is C_4H_9Cl.

(ii) Compound '*B*' reacts with NH_3, to form amine '*C*'.

$$\underset{A}{C_4H_8} \xrightarrow{HCl} \underset{B}{C_4H_9Cl} \xrightarrow{NH_3} \underset{C}{C_4H_{11}N} \text{ or } C_4H_9NH_2$$

(iii) '*C*' gives diazonium salt with $NaNO_2$ / HCl, which yields an optically active alcohol. So, '*C*' is an aliphatic amine.

(iv) '*A*' on ozonolysis produces 2 moles of CH_3CHO. So, '*A*' is $CH_3-CH=CH-CH_3$ (but-2-ene).

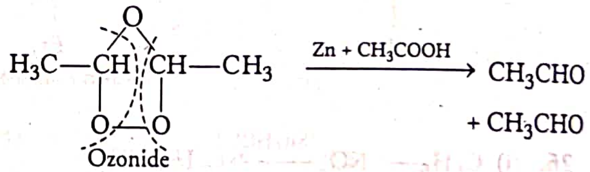
Therefore, overall reaction sequence looks like

(i) $$\underset{\text{But-2-ene (A) }(C_4H_8)}{\overset{4}{C}H_3-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_3} \xrightarrow{HCl} \underset{\text{2-chlorobutane (B) }(C_4H_9Cl)}{\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H(Cl)-\overset{1}{C}H_3}$$

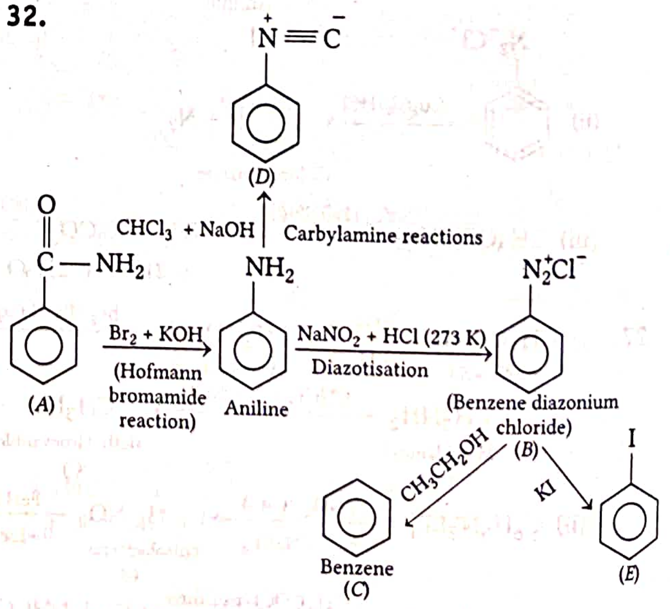
(ii) $$\underset{\text{2-chlorobutane [B]}}{CH_3-CH_2-CH(Cl)-CH_3} \xrightarrow{NH_3} \underset{\text{2-aminobutane (C) }(C_4H_{11}N)}{CH_3-CH_2-CH(NH_2)-CH_3}$$

(iii) $$\underset{\text{2-aminobutane (C) }(C_4H_{11}N)}{CH_3-CH_2-CH(NH_2)-CH_3} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } NaNO_2/HCl} \underset{\text{Butan-2-ol (D) (Optically active)}}{CH_3-C(H)(OH)-CH_2CH_3}$$

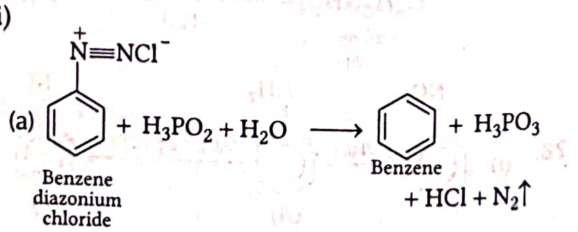
(iv) $CH_3-CH=CH-CH_3 + O_3 \longrightarrow$

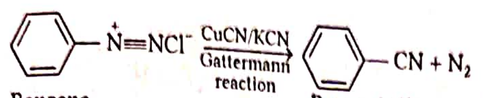


32.

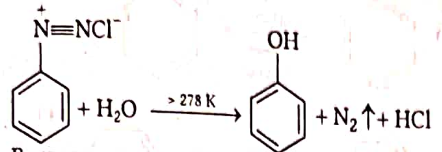


33. (i)



(b) 

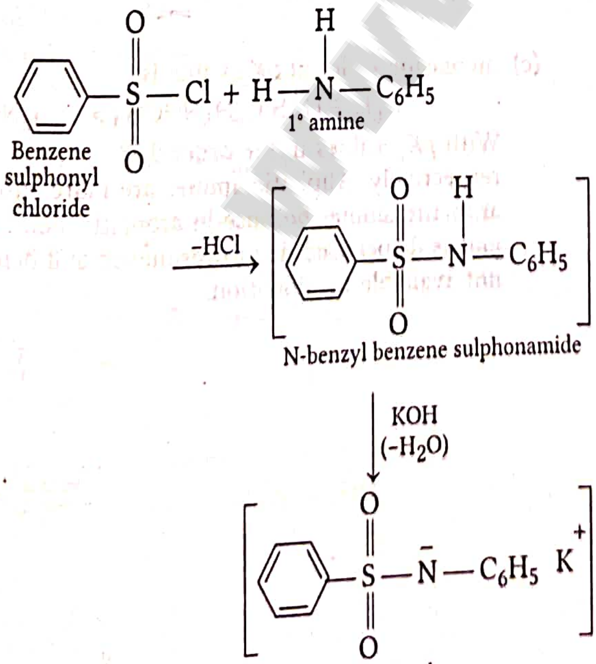
Benzene diazonium chloride — Benzonitrile

(c) 

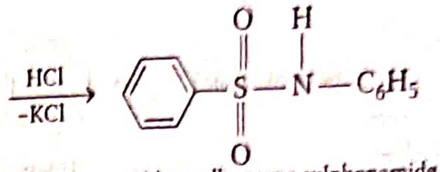
Benzene diazonium chloride — Phenol

(ii) The relative basic strength of $C_2H_5NH_2$, $(C_2H_5)_2NH$ and $(C_2H_5)_3N$ depends upon the stabilisation of their corresponding conjugate acids formed as a result of accepting a proton from water by a number of factors such as H-bonding, steric hindrance created by the alkyl groups and + *I*-effect of the alkyl groups. All these factors are favourable for 2° amines, therefore, $(C_2H_5)_2NH$ is a stronger base than $C_2H_5NH_2$ and $(C_2H_5)_3N$. Since, $(C_2H_5)_3$ group is large, it exerts some steric hindrance to H-bond. Thus, $(C_2H_5)_3N$ is more basic than $C_2H_5NH_2$. Hence, the overall basic strength of the three amines in aqueous medium increases in the order : $C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$

(iii) The given amines are primary and secondary aromatic amines. In order to distinguish between primary and secondary amine, the amine is shaken with benzene sulphonyl chloride (Hinsberg's reagent) in the presence of excess of aqueous KOH solution. A primary amine gives a clear solution which on acidification gives an insoluble N-alkyl benzene sulphonamide.

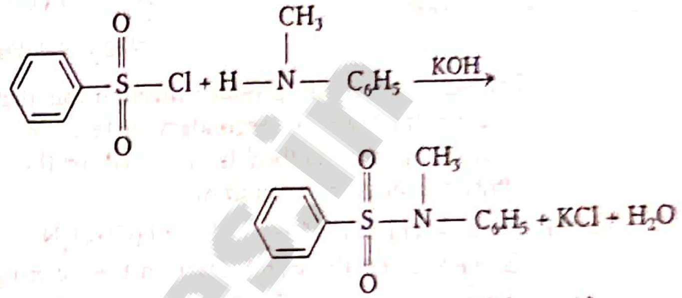


Benzene sulphonyl chloride; 1° amine; N-benzyl benzene sulphonamide; Potassium salt (Soluble in KOH)



N-benzylbenzene sulphonamide (Insoluble in HCl)

A secondary amine gives an insoluble N, N-dialkyl benzene sulphonamide which remains unaffected on addition of acid.



N-benzyl-N-methyl benzene sulphonamide (Insoluble in KOH)

34. (a)(i) **Hofmann Bromamide Degradation Reaction** This reaction is used for preparing amine containing one carbon less than the starting amide. This method was developed for the preparation of primary amines by reacting an amide with Br_2/Cl_2 in NaOH/KOH. In this reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the N-atom.

$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

e.g. $$\underset{\text{Amide}}{CH_3CH_2CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Amine}}{3CH_3CH_2NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

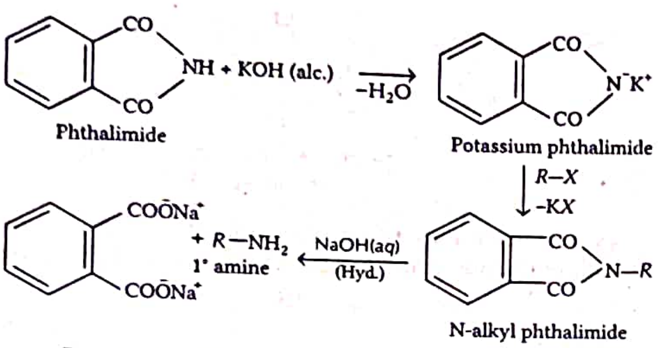
(ii) **Diazotisation** The conversion of primary aromatic amines into their diazonium salts is called diazotisation.

Benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid (which is produced by the reaction of $NaNO_2$ and HCl) at 273-278 K or 0-5°C as shown below:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278\,K} C_6H_5\overset{+}{N_2}\overset{-}{Cl} + NaCl + 2H_2O$$

Due to its unstability, the diazonium salt is not generally stored and is used immediately after its preparation.

(iii) **Gabriel Phthalimide Synthesis** When a phthalimide is treated with ethanolic KOH, it forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis forms corresponding primary amines as shown below.

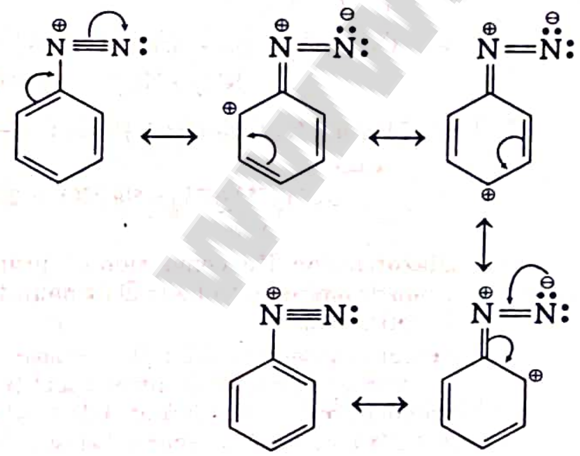


Primary amines are produce through this method without the traces of secondary or tertiary amines. So, this method is preferred for the synthesis of primary amines.

(b) (i) Basic strength of $(CH_3)_2NH$ and $(CH_3)_3N$ depends upon the stabilisation of their conjugate acids by a number of factors such as H-bonding, steric hindrance of alkyl groups and $+I$-effect of alkyl groups.

The first two factors are favourable for 2° amines, hence $(CH_3)_2NH$ is a stronger base than $(CH_3)_3N$ in aqueous medium.

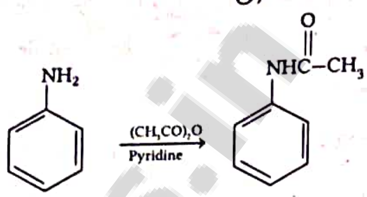
(ii) Diazonium salts of aromatic amines are more stable than those of aliphatic amines due to the delocalisation of the positive charge on the benzene ring as shown below by the resonating structures.



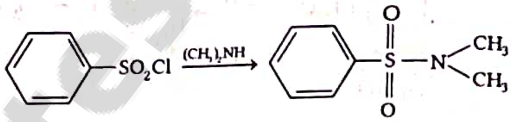
Or

(a)

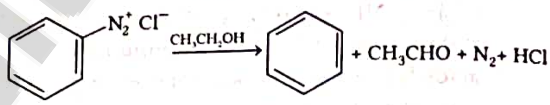
(i)



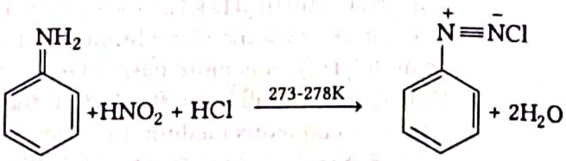
(ii)



(iii)

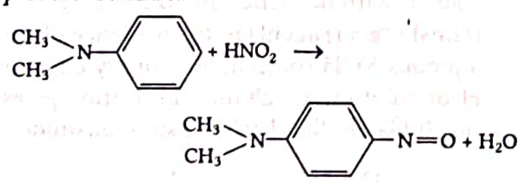


(b) Aniline and N, N-dimethyl aniline can be distinguished using reaction with nitrous acid. Aniline is primary aromatic amine, it reacts with nitrous acid at low temperature forming arene diazonium salt.



Benzene diazonium chloride

N, N-dimethylamine is tertiary aromatic amine, it reacts with nitrous acid to form green coloured *p*-nitrosoamine.



(c) Increasing order of pK_b value is

$$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2$$

With pK_b values in the order 9.38 > 9.30 > 3.29 respectively. Aliphatic amines are more basic than aromatic amines because in aromatic amine the lone pair is delocalised due to resonance and hence, it is not available for donation.

SUMMARY

- Amines are formed by the replacement of H of ammonia by alkyl/aryl group.
- Amines are classified as : 1° amine (RNH_2), 2° amine (R_2NH) and 3° amine (R_3N)
- Methods of preparation of amines are

(i) Reduction of $-NO_2$, $-NO_2 \xrightarrow[\text{Metal + acid}]{\text{Raney Ni/Pt}} -NH_2$

(ii) Reduction of $-CN$ or $-CONH_2$

$-CN \xrightarrow{LiAlH_4} -CH_2NH_2$ or $-CONH_2$

(iii) Hofmann Bromamide Reaction

$-CONH_2 \xrightarrow[Br]{NaOH} -NH_2$

(iv) Hofmann Ammonolysis

$NH_3 \xrightarrow[-HX]{RX} RNH_2\ (1°)$

$\downarrow RX$

$\underset{(3°)}{R_3N} \xleftarrow{RX} \underset{(2°)}{R_2NH}$

(v) Gabriel-Phthalimide Reaction

Phthalimide $\xrightarrow{KOH}$ K salt of phthalimide

$\downarrow RX$

1°amine (aliphatic) $\xleftarrow{NaOH}$ N-alkyl phthalimide

- Their solubility decreases but boiling point increases with increase in molecular mass.
  - The order of bp is 1° > 2° > 3° amines.
  - The order of basicity
    (i) In gaseous state is 3°amine > 2°amine > 1° amine.
    (ii) In aqueous solution is 2°amine > 3°amine > 1°amine > NH_3, If $R = C_2H_5$ and 2° > 1° > 3° > NH_3 if $R = CH_3$.
- The chemical reactions of amines are

(i) $\boxed{\underset{(1°)}{R-NH_2}} \xrightarrow[\text{Acylation}]{RCOCl} R-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-R'$ Substituted amide

$\xrightarrow[\text{Carbylamine reaction}]{CHCl_3 + KOH} R-NC$

$\xrightarrow[\text{Hinsberg's reagent}]{C_6H_5SO_2Cl}$ N-alkylbenzene sulphonamide (soluble in alkali)

(ii) $\boxed{R_2NH\ (2°)} \xrightarrow[\text{reagent}]{\text{Hinsbergs}}$ N,N-dialkylbenzene sulphonamide (insoluble in alkali)

(iii) $\boxed{R_3N\ (3°)} \xrightarrow{C_6H_5SO_2Cl}$ No reaction

(iv) $\boxed{RNH_2} \xrightarrow[\text{(Here, } R = C_6H_5)]{\text{Electrophilic substitution}}$

(Here, $R = C_6H_5$)

$\xrightarrow[H_2O]{Br_2}$ 2,4,6-tribromoaniline

$\xrightarrow[Br_2]{(CH_3CO)_2O}$ p-bromoaniline

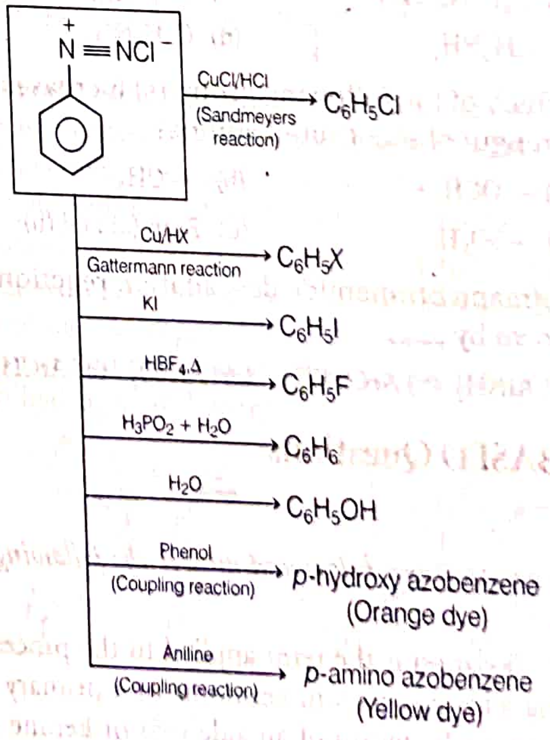
$\xrightarrow[H_2SO_4]{HNO_3}$ m + o + p-nitroaniline (47%) (2%) (51%)

- The formula of diazonium salts is $C_6H_5N{=}N^+Cl^-$.
- It is prepared as follows :

$$\underset{\text{1°amine (aromatic)}}{C_6H_5-NH_2} \xrightarrow[\text{or } NaNO_2 + HCl,\ 0°C]{HNO_2} \underset{\text{Diazonium salt}}{C_6H_5\overset{+}{N_2}Cl^-}$$

- They are colourless, unstable, soluble in water and neutral to litmus.

The chemical reactions of amines are



CHAPTER PRACTICE

OBJECTIVE Type Questions

1 $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-NH_2$ is a

(a) primary amine (b) secondary amine
(c) tertiary amine (d) None of these

2 In the reaction $C_6H_5CONH_2 \xrightarrow[\Delta]{Br_2 + KOH}$ Major product A is

(a) C_6H_6 (b) C_6H_5CHO
(c) $C_6H_5NH_2$ (d) C_6H_5COOKI

3 Out of the following which one react with $NaNO_2 + HCl$ to form alcohol

(a) $C_6H_5NHCH_3$ (b) $(CH_3)_2NH$
(c) CH_3NH_2 (d) $C_6H_5NH_2$

4 Which of the following group (s) increases basic strength of substituted aniline?

(a) $-OCH_3$ (b) $-CH_3$
(c) $-SO_3H$ (d) Both (a) and (b)

5 Hofmann bromamide degradation reaction is shown by ....

(a) $ArNH_2$ (b) $ArCONH_2$ (c) $ArNO_2$ (d) $ArCH_2NH_2$

CASE BASED Questions

Case I

(Read the passage given below and answer the following questions)

Reductive alkylation is the term applied to the process of introducing alkyl groups into ammonia or a primary or secondary amine by means of an aldehyde or ketone in the presence of a reducing agent. The present discussion is limited to those reductive alkylations in which the reducing agent is hydrogen and a catalyst or "nascent" hydrogen, usually from a metalacid combination; most of these reductive alkylations have been carried out with hydrogen and a catalyst.

The principal variation excluded is that in which the reducing agent is formic acid or one of its derivatives; this modification is known as the Leuckart reaction. The process of reductive alkylation of ammonia consists in the addition of ammonia to a carbonyl compound and reduction of the addition compound or its dehydration product.

The reaction usually is carried out in ethanol solution when the reduction is to be effected catalytically

$$RCHO + NH_3 \rightleftharpoons RCHOHNH_2 \xrightarrow{2[H]} RCH_2NH_2$$
$$RCHOHNH_2 \rightleftharpoons RCH{=}NH \xrightarrow{2[H]} RCH_2NH_2$$

Since the primary amine is formed in the presence of the aldehyde it may react in the same way as ammonia, yielding an addition compound, a Schiff's base ($RCH{=}NCH_2R$) and finally, a secondary amine. Similarly, the primary amine may react with the imine, forming an addition product which also is reduced to a secondary amine Finally, the secondary amine may react with either the aldehyde or the imine to give products which are reduced to tertiary amines.

$$RCH{=}NH + RCH_2NH_2 \rightleftharpoons \underset{\displaystyle NH_2}{\underset{|}{RCHNHCH_2R}} \xrightarrow{2[H]} (RCH_2)_2NH + NH_3$$

$$(RCH_2)_2NH + RCHO \rightleftharpoons (RCH_2)_2N\underset{\displaystyle OH}{\underset{|}{CHR}} \xrightarrow{2[H]} (RCH_2)_3N + H_3O$$

$$(RCH_2)_2N + RCH{=}NH \rightleftharpoons (RCH_2)_2N\underset{\displaystyle NH_2}{\underset{|}{CHR}} \xrightarrow{2[H]} (RCH_2)_3N + NH_3$$

Similar reactions may occur when the carbonyl compound employed is a ketone.

6 Ethanal on reaction with ammonia forms an imine (X) which on reaction with nascent hydrogen gives (Y). Identify 'X' and 'Y'.
(a) X is $CH_3CH{=}NH$ and Y is CH_3NH_2
(b) X is $CH_3CHOHNH_2$ and Y is $CH_3CH_2NH_2$
(c) X is $CH_3CHOHNH_2$ and Y is CH_3NH_2
(d) X is $CH_3CH{=}NH$ and Y is $CH_3CH_2NH_2$

7 Acetaldehyde is reacted with ammonia followed by reduction in presence of hydrogen as a catalyst. The primary amine so formed further reacts with acetaldehyde. The Schiff's base formed during the reaction is
(a) $CH_3CH{=}NHCH_3$ (b) $CH_3CH{=}NHCH_2CH_3$
(c) $CH_3{=}NHCH_2CH_3$ (d) $CH_3CH_2CH{=}NHCH_3$

8 The reaction of ammonia and its derivatives with aldehydes is called
(a) nucleophilic substitution reaction
(b) electrophilic substitution reaction
(c) nucleophilic addition reaction
(d) electrophilic addition reaction

9 $(CH_3CH_2CH_2)_2NH + CH_3CH_2CHO \longrightarrow P \xrightarrow{2[H]} Q$
The compound Q is
(a) $(CH_3CH_2CH_2)_3N$
(b) $(CH_3CH_2CH_2)_2N(CH_2CH_3)$
(c) $(CH_3CH_2)_3N$
(d) $(CH_3CH_2)_2NH$

Or Reductive alkylation of ammonia by means of an aldehyde in presence of hydrogen as reducing agents results in formation of
(a) primary amines
(b) secondary amines
(c) tertiary amines
(d) mixture of all three amines

Case II

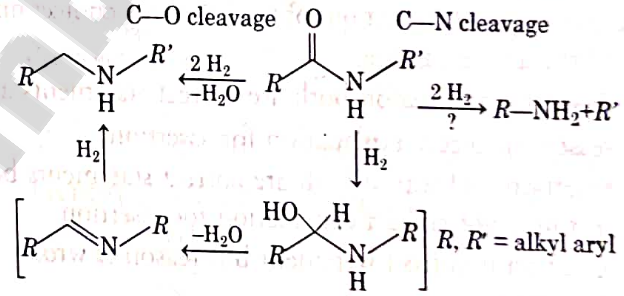
Reduction of carboxylic acids and their derivatives plays an important role in organic synthesis, in both laboratory and industrial processes. Traditionally, the reduction is performed using stoichiometric amounts of hydride reagents, generating stoichiometric amounts of waste.

A much more attractive, atom-economical approach is a catalytic reaction using H_2; however, hydrogenation of carboxylic acid derivatives under mild conditions is a very challenging task, with amides presenting the highest challenge among all classes of carbonyl compounds.

Very few examples of the important hydrogenation of amides to amines, in which the C—O bond is cleaved with the liberation of water (Scheme 1), were reported. C—O cleavage of amides can also be affected with silanes as reducing agents. In addition, the interesting hydrogenation of cyclic N-acylcarbamates and N-acylsulfonamides, which involves cleavage of the C—N bond, but does not form amines, was recently reported by Ikariya.

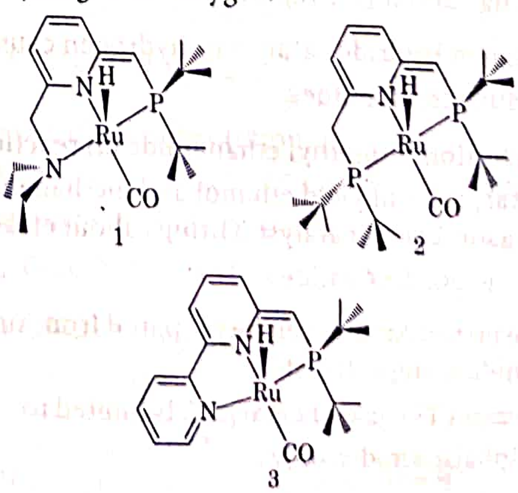
On the other hand, to the best of our knowledge, selective, direct hydrogenation of amides to form amines and alcohols has not been reported. Amines and alcohols are used extensively in the chemical, pharmaceutical, and agrochemical industries. Design of such a reaction is conceptually challenging, since the first mechanistic step in amide hydrogenation is expected to be H_2 addition to the carbonyl group to form a very unstable hemiaminal which, in the case of primary or secondary amides, spontaneously liberates water to form an imine; further hydrogenation of the imine then leads to amine formation (Scheme 1). This is the basis of the amide hydrogenation mentioned above. For amine and alcohol formation, cleavage of the C—N bond in preference to the C—O bond would be required. **CBSE Question Bank**

Scheme 1. General Scheme for Hydrogenation of Amides



(Figure 1) efficiently catalyses the dehydrogenative coupling of alcohols to form esters, the hydrogenation of esters to alcohols under mild conditions and the novel coupling of alcohols and amines to form amides and H_2.

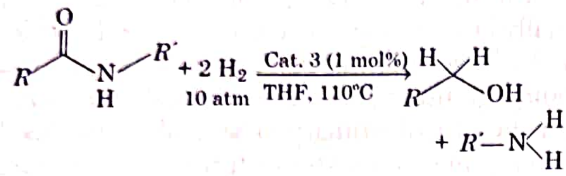
The dearomatised PNP complex 2 is an efficient catalyst for the dehydrogenative coupling of alcohols and amines to form imines. Complex 1 is also effective in N—H activation and in the unique light-induced splitting of water to hydrogen and oxygen.



Dearomatized Ru-pincer complex

We have now prepared the new, dearomatised, bipyridine-based pincer complex 3. Remarkably, 3 efficiently catalyses the selective hydrogenation of amides to form amines and alcohols (Eq 1).

The reaction proceeds under mild pressure and neutral conditions, with no additives being required. Since, the reaction proceeds well under anhydrous conditions, hydrolytic cleavage of the amide is not involved in this process.



R = Aryl and alkyl and R' = Aryl, alkyl and aryalkyl

Direct Hydrogenation of Amides to Alcohols and Amines under Mild Conditions

In the following questions, a statement of assertion followed by a statement of reason is given.

Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

10 **Assertion** The use of catalyst 3 is an efficient method of preparation of primary amines

Reason Use of catalyst 3 is a step down reaction.

11 **Assertion** Use of hydride catalyst or hydrogen brings about cleavage of C—O bond in amides.

Reason Hydride catalyst or hydrogen cause to reduction of amides.

12 **Assertion** N-methyl ethanamide on reaction with catalyst 3 will yield ethanol and methanamine.
Reason Use of catalyst 3 brings about cleavage of C—N bond of amides

13 **Assertion** Aniline can be prepared from suitable amide using catalyst 3.

Reason The use of catalyst 3 is limited to aliphatic amides only.

ASSERTION and REASON

■ **Directions** (Q. Nos. 14-19) *In the following questions, an Assertion (A) is followed by a corresponding Reason (R) Use the following keys to choose the appropriate answer.*

(a) Both (A) and (R) are correct, (R) is the correct explanation of (A).
(b) Both (A) and (R) are correct, (R) is not the correct explanation of (A).
(c) (A) is correct; (R) is incorrect.
(d) (A) is incorrect; (R) is correct.

14 **Assertion** (A) Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.

Reason (R) Aryl halides do not undergo electrophilic substitution with anion formed by phthalimide.

15 **Assertion** (A) In acylation reaction of amines, equilibrium shifts to the right hand side in the presence of pyridine.

Reason (R) In the presence of strong base, HCl is removed and reaction shifts toward the right hand side.

16 **Assertion** (A) Aniline does not undergo alkylation and acetylation.

Reason (R) Nitrogen of aniline acquires positive charge in the presence of $AlCl_3$.

17 **Assertion** (A) Benzene diazonium salts are soluble in water.

Reason (R) They are covalent in nature, so they are soluble in water.

18 **Assertion** (A) Tertiary butyl amine can be prepared by the action of NH_3 on *tert*-butyl bromide.

Reason (R) Tertiary butyl bromide being 3° alkylhalide prefers to undergo elimination on the treatment with a base.

19 **Assertion** (A) Acetanilide is less basic than aniline

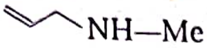
Reason (R) Acetylation of aniline results in decrease in decrease of electron density of nitrogen.

VERY SHORT ANSWER Type Questions

20 Why does trimethylamine have an angle of 108°?

21 Draw the structure of N, N-*bis* (1-bromo ethyl) ethanamine.

22 Write the IUPAC nomenclature of the compound.

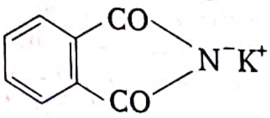


23 Name the reagent that reacts with nitromethane to form methyl hydroxylamine.

24 Find out the incorrect names and correct them.

(a) N-butylaminoethane (b) 1-amino 2-ethanol
(c) methylaniline (d) propanediamine
(e) 1-phenylaminoethane

25 Give the structure of *A* in the following reaction:

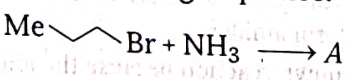
A + alc.KOH $\xrightarrow[-H_2O]{}$ 

26 What is the number of 1° H-atoms present in an amine, obtained by reduction of benzamide?

27 Account for the following:

Ammonolysis of alkyl halide does not give a corresponding amine in pure state.

28 Write *A* in the following sequence:



29 Reduction of nitrobenzene depends upon pH. Give reason.

30 How can you convert an amide into amine having one carbon atom less than the starting compound?

31 What happens when nitroethane is treated with $LiAlH_4$?

SHORT ANSWER Type I Questions

32 (i) *Tert*-butylamine cannot be prepared by the action of NH_3 on *tert*-butylbromide. Give reason.

(ii) How is aminomethane obtained from ethanal?

33 Account for the following :

(i) Amines are basic substances while amides are neutral.

(ii) Aromatic amines are weaker bases than aliphatic amines.

34 (i) Under what conditions, aniline gives *p*-nitro derivative as the major product?

(ii) Write the IUPAC name of the product formed when nitrobenzene is reduced using tin and concentrated hydrochloric acid.

35 Why the hydrogen atoms of the methyl group in *o*-and *p*-nitrotoluenes are acidic in nature while those of toluene are not?

36 How will you convert cyclohexane carboxamide to N-methyl cyclohexylamine?

37 Which is the best method for preparing primary amines from alkyl halides, without changing the number of carbon atoms in the chain? Give mechanism.

38 How will you distinguish between the following pairs of compounds?

(i) Ethylamine and trimethylamine

(ii) Aniline and N-methylaniline

39 Why does aliphatic amines are more reactive towards hydrochloric acid as comparison to arylamine?

40 What happens when

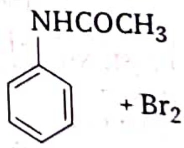
(i) toluene is treated with conc. HNO_3 and conc. H_2SO_4 at 293 K?

(ii) nitrobenzene is treated with conc. HNO_3 and conc. H_2SO_4 at 363 K?

41 $\underset{\substack{\text{(Optically active)} \\ (X)}}{C_5H_{13}N} \xrightarrow[HCl]{aq\ NaNO_2} \underset{\substack{3° \\ \text{alcohol}}}{Y}$ + Other products

(i) Identify *X* and *Y*. (ii) Is *Y* optically active?

42 Identify the product of the following reaction:

 $+ Br_2/CH_3COOH \longrightarrow$

43 Usually, benzene diazonium salts are unstable but benzene diazonium fluoroborate is stable. Why?

44 Draw the resonating structures of benzene diazonium salt.

45 Aniline is diazotised in cold and then treated with dimethylaniline to give a coloured product. What is the structure of this product?

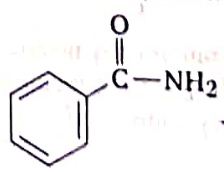
SHORT ANSWER Type II Questions

46 Electrophilic substitution in case of aromatic amines takes place more readily than benzene.

47 Complete the following reactions.

(i) $CH_3CH_2NH_2 + CHCl_3 +$ (alc.)KOH $\longrightarrow$

(ii) $C_6H_5N_2^+Cl^- \xrightarrow[\text{(Room temp.)}]{H_2O}$

(iii)  $\xrightarrow{H_3O^+} A \xrightarrow{\Delta} B$

48 Why does bromination of aniline, even under very mild conditions, gives 2, 4, 6- tribromoaniline instantaneously?

49 Identify A and B in the following reactions.

(i) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CONH_2 \xrightarrow{Br_2,\, NaOH} A \xrightarrow{HNO_2} B$

(ii) $C_6H_5NO_2 \xrightarrow{Br_2/Fe^{3+}} A \xrightarrow{HNO_2} B$

(iii) $CH_3CN \xrightarrow{H^+, H_2O} A \xrightarrow{LiAlH_4} B$

50 (i) What are coupling reactions? How does the electrophilic substitution reaction take place during this reaction?

(ii) List some important applications of diazonium salts.

ANSWERS

1. (a) **2.** (c) **3.** (c) **4.** (d) **5.** (b)

6 (d)

$$\underset{\text{(Ethanal)}}{CH_3CHO} + \underset{\text{(Ammonia)}}{NH_3} \longrightarrow H_2N-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{-H_2O} \underset{\text{(Imine)} \quad (X)}{HN{=}CH-CH_3} \xrightarrow{+2(H)} \underset{\substack{(Y) \\ \text{(Ethanamine)}}}{CH_3CH_2NH_2}$$

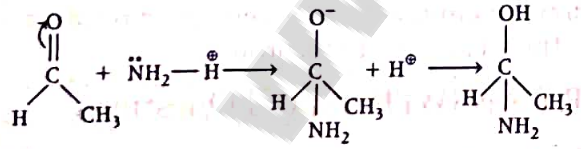
7 (b)

$$CH_3CHO + NH_3 \longrightarrow H_2N-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{-H_2O} \underset{\text{Imine}}{HN{=}CH-CH_3} \xrightarrow{+2(H)} \underset{\text{Amine}}{CH_3CH_2NH_2}$$

$$CH_3CH_2NH_2 \xrightarrow{+CH_3CHO} \underset{\text{(Schiff's base)}}{H_3C-CH_2N{=}CH-CH_3} + H_2O$$

8 (c) The reaction of ammonia and its derivatives with aldehydes is called nucleophilic addition reaction.

Complete reaction is as follows



9 (a)

$$(CH_3CH_2CH_2)_2NH + CH_3CH_2CHO \longrightarrow \underset{(P)}{(CH_3CH_2CH_2)_2N-\underset{\underset{OH}{|}}{CH}CH_2CH_3} \xrightarrow{+2(H)} \underset{(Q)}{(CH_3CH_2CH_2)_3N} + H_2O$$

Or (a) Reductive alkylation of ammonia by means of an aldehyde in presence of hydrogen as reducing agent result in formation of primary amine.

$$CH_3CHO + NH_3 \longrightarrow CH_3\overset{\overset{OH}{|}}{CH}-NH_2 \xrightarrow{-H_2O} CH_3-CH{=}NH \xrightarrow{+2(H)} \underset{\text{(Primary amine)}}{CH_3CH_2NH_2}$$

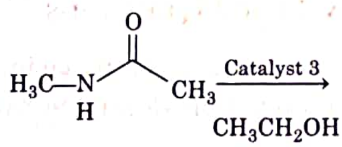
10 (b) Catalyst 3 is bipyridine-based pincer complex-3. It efficiently catalyses the selective hydrogenation of amides to form amines.

It is a step down reaction because the amine formed contains one carbon less than that present in the amide,

11 (b) Use of hydride catalyst is also known as hydrogenation.

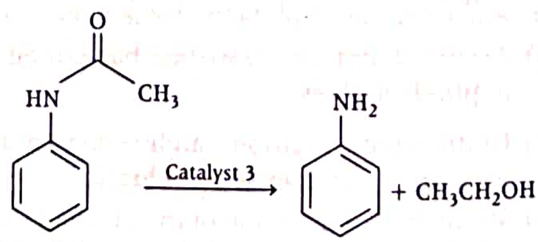
Hydrogenation can be used to reduce amides to amines; however, the process often requires high Pressure (197 atm) and temperature (200°C).

12 (a) When we use catalyst 3, it cleaved C—N bond of amides. So, N-methyl ethanamide on reaction with catalyst 3 will yield ethanol and methanamine.



$$\underset{\text{(Ethanol)}}{CH_3CH_2OH} + \underset{\text{(Methanamine)}}{CH_3NH_2}$$

13 (c) Aniline can be prepared from suitable amide using catalyst 3.



(Acetanilide) (Aniline)

Catalyst 3 can be used for aliphatic amides as well as aromatic amides.

14 (c) Aromatic primary amines cannot be prepared by the Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution reaction with the anion formed by phthalimide. Thus, (A) is correct but (R) is incorrect.

15 (a) In acylation reaction of amines, equilibrium shifts to the right side in the presence of pyridine because it is a stronger base than amine which removes HCl so formed in the reaction.

Thus, both (A) and (R) are correct and (R) is the correct.

16 (a) Aniline does not undergo Friedel Crafts reaction (alkylation and acetylation) due to salt formation with $AlCl_3$, (the Lewis acid) which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence, acts as a strong deactivating group for further reaction. Thus, both (A) and (R) are correct and (R) is the correct.

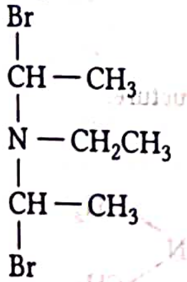
17 (c) Benzene diazonium salts are soluble in water because they are ionic in nature. Thus, (A) is correct and R is incorrect.

18 (d) Tertiary butyl amine cannot be prepared by the action of NH_3 on tert-butyl bromide. Because *tert*-butyl bromide prefer to undergo elimination rather than substitution on treatment with a base. The product is *iso*-butylene rather than *tert*-butylamine. Hence, (A) is incorrect but (R) is correct.

19 (a) Both A and R are correct and R is the correct explanation of A.

20 Due to the presence of unshared pair of electrons, the angle C — N — C is less than 109.5°.

21

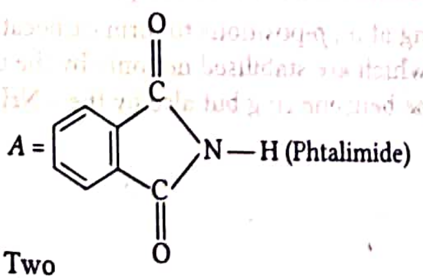


22 N-methylpropene

23 Reducing agent, Fe, Sn/HCl

24 (a) N-ethylbutanamine (b) 2-amino ethanol (c) 2-aminotoluene (e) 1-phenyl ethanamine

25



26 Two

27 **Hint** Formation of quaternary ammonium salt. Refer to text on page 363.

28

29 Aromatic nitro compounds can be reduced to variety of products.

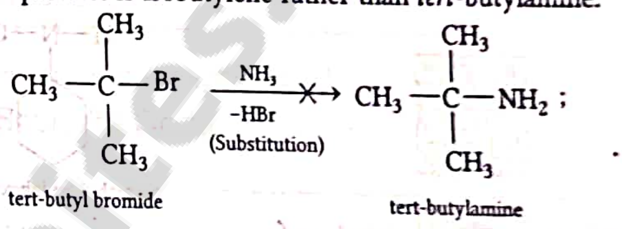
$$C_6H_5NO_2 \xrightarrow{-O} C_6H_5NO \xrightarrow{2H} C_6H_5NHOH \xrightarrow{-O} C_6H_5NH_2$$

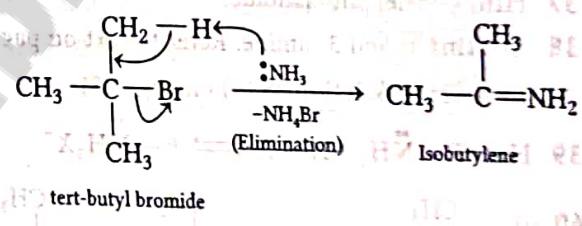
The nature of final product of reduction depends on the pH of the reducing medium.

30 By Hofmann bromamide degradation

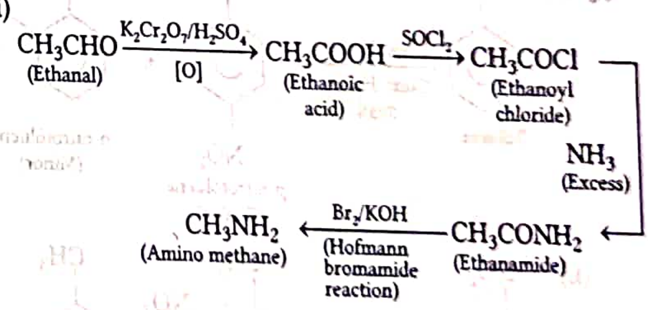
31 $C_2H_5NO_2 \xrightarrow{LiAlH_4} C_2H_5NH_2$

32 (i) *tert*-butyl bromide, being a 3° alkyl halide, on treatment with a base (i.e. NH_3) prefers to undergo elimination rather than substitution. Therefore, the product is isobutylene rather than *tert*-butylamine.

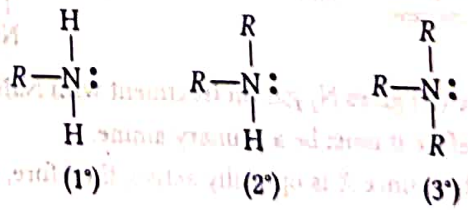




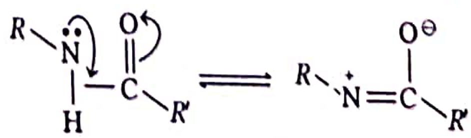
(ii)



33 (i) Amines are basic because in amines lone pair of electrons on nitrogen is free to act as base.



But in amides, the lone pair on nitrogen is involved in conjugation with adjacent carbonyl group. Now, it is no longer in condition to donate its lone pair of electrons to act as a base. This is the reason it is neutral.



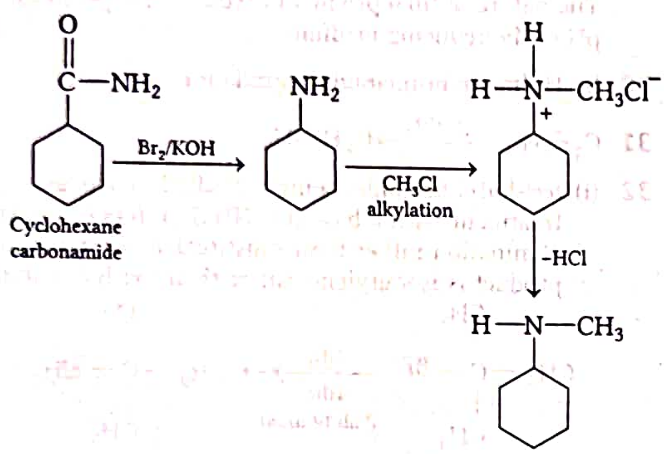
(ii) Refer to text on page 371.

34 (i) Refer to text on pages 373 and 374.

(ii) **Hint** Benzenamine.

35 **Hint** Due to the presence of electron withdrawing group in *o*-and *p*- nitro toluene.

36



N-methyl cyclohexylamine

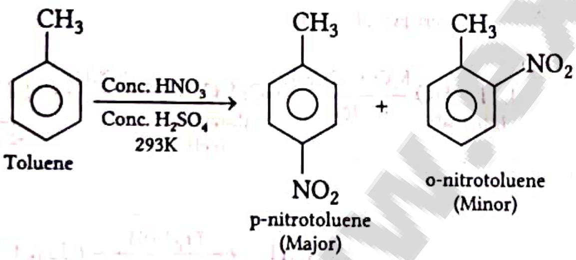
37 **Hint** Gabriel phthalamide.

38 (i) **Hint** 1° and 3° amine. Refer to text on page 372.

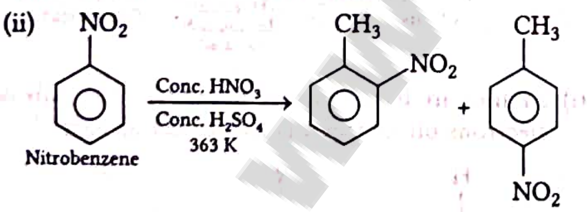
(ii) Refer to Solution 38 (ii) on page 381.

39 **Hint** $R—\ddot{N}H_2 + H—X \rightleftharpoons R—\overset{+}{N}H_3X^-$

40 (i)



(ii)

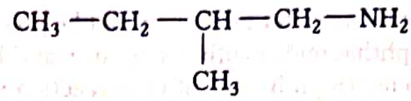


41 Since (*X*) gives N_2 gas on treatment with $NaNO_2/HCl$, therefore it must be a primary amine.

Further, since *X* is optically active, therefore, it possess chiral structure.

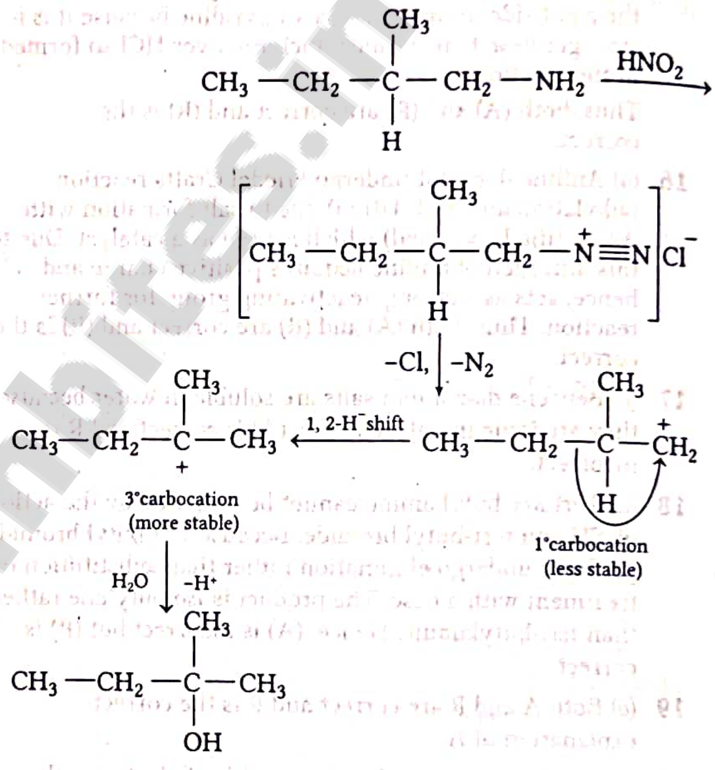
Now, NH_2 group cannot be directly attached to the chiral carbon because such amines readily undergoes racemisation due to inversion at N-atom.

Therefore, the probable structure of *X* is



2-methyl butanamine (*X*)
(optically active)

To determine the structure of 3° alcohol (*Y*)



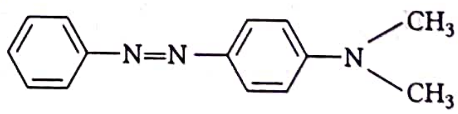
2-methyl butan-2-ol
(*Y*) (optically inactive)

42 Refer to text on page 373.

43 **Hint** On the basis of resonance structure.

44 Refer to text on page 386.

45 **Hint**

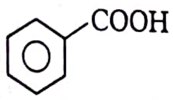
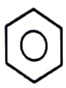


46 Due to strong electron donating effect of the $-NH_2$ group, the electron density increases at the *o*-, *p*- positions.

Further, when aniline is treated with Br_2, the Br^+ attacks the benzene ring at *o*-, *p*-positions to form carbocation intermediates which are stabilised not only by the usual resonance of the benzene ring but also by the $-NH_2$ group.

47 (i) Refer to text on page 372.

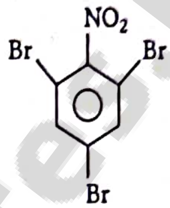
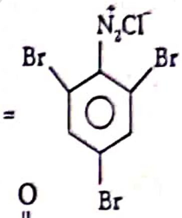
(ii) Refer to text on page 372.

(iii) **Hint :** $A =$  , $B =$ 

48 Refer to text on page 373.

49 (i) $A = CH_3CH(CH_3)\ NH_2$

$B = CH_3CH\ (CH_3)\ N_2^+Cl^-$

(ii) $A =$  $B =$ 

(iii) $A = CH_3COOH,\ B = CH_3\overset{\overset{\displaystyle O}{\|}}{C}—NH_2$

50 (i) Refer to text on page 386.

(ii) Refer to text on page 387.

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10

BIOMOLECULES

The most incredible aspect of a living system is that it grows, sustains and reproduces itself. Our living system is composed of non-living atoms and molecules.The study of various chemical changes taking place within the living system falls in the domain of biochemistry.

All living systems are composed of various complex organic compounds namely carbohydrates, proteins, fats or lipids and nucleic acids. These organic compounds are referred to as biomolecules. Carbohydrates and proteins are the essential constituents of our food. In addition, some simple molecules like vitamins and mineral salts also play an important role in the functioning of organisms.

CHAPTER CHECKLIST

- Carbohydrates
- Proteins and Enzymes
- Vitamins, Nucleic Acid and Hormones

|TOPIC 1|

Carbohydrates

These are primarily produced by plants and form a very large group of naturally occurring organic compounds. Most of them have a general formula, $C_x(H_2O)_y$ and were considered as hydrates of carbon from where the name carbohydrate was derived, e.g. the molecular formula of glucose ($C_6H_{12}O_6$) fits into the given general formula, $C_6(H_2O)_6$. But all the compounds which fit into this formula may not be classified as carbohydrates, e.g. acetic acid (CH_3COOH). Similarly, all the carbohydrates do not fit into this formula, e.g. rhamnose ($C_6H_{12}O_5$) is a carbohydrate but does not fit in the formula.

A large number of chemical reactions have shown that they contain specific functional groups. Thus, chemically, the carbohydrates may be defined as **optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis.** Some of the carbohydrates are sweet in taste which are also called sugars. These constitute an important class of compounds like glucose, fructose, sucrose, starch, cellulose, etc., which play a vital role in our daily life. Carbohydrates are also known as **saccharides**.

Classification of Carbohydrates

On the basis of the behaviour towards hydrolysis, carbohydrates are broadly classified into the following three classes :

Monosaccharides

Simple carbohydrates which are composed of single unit of saccharide and cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone, are called monosaccharides. It may consist upto six carbon atoms. About twenty monosaccharides are known to occur in nature, e.g. glucose, fructose, ribose, etc.

Oligosaccharides

Carbohydrates which give 2-10 monosaccharide units on hydrolysis are called oligosaccharides. They can be grouped further into di, tri, tetrasaccharides, etc., depending upon the actual number of monosaccharide units they give on hydrolysis. Amongst these, the most common are disaccharides. The two monosaccharide units obtained on hydrolysis of a disaccharide may be same or different, e.g. sucrose gives one molecule each of glucose and fructose whereas maltose gives two molecules of glucose only.

Polysaccharides

Carbohydrates which give a large number of monosaccharide units on hydrolysis are called polysaccharides, e.g. starch, cellulose, glycogen, etc. These are not sweet in taste, therefore they are called **non-sugars.**

On the basis of reducing activity, carbohydrates can be classified as follows :

Reducing Sugars

Carbohydrates in which ketonic or aldehydic groups are free and are capable of reducing Fehling's solution or Tollen's reagent are known as reducing sugars, e.g. monosaccharides like glucose, fructose, ribose, etc.

Non-reducing Sugars

Carbohydrates in which aldehydic or ketonic group are bonded and are not capable of reducing Fehling's solution or Tollen's reagent are called non-reducing sugars, e.g. disaccharides like sucrose and polysaccharides like starch, cellulose, glycogen, dextrins, etc.

Classification of Monosaccharides

On the basis of number of carbon atoms and the functional group present in them, monosaccharides are further classified as :

(i) **Aldose** If aldehyde (—CHO) group is present in monosaccharides, then it is called aldose, e.g. sugar containing 3, 4, 5 carbon atoms are aldotriose, aldotetrose and aldopentose, respectively.

(ii) **Ketose** If monosaccharides contain keto ($>C=O$) group, then it is called ketose, e.g. sugar containing 3, 4, 5 carbon atoms are ketotriose, ketotetrose and ketopentose, respectively.

Glucose

It is an aldohexose and occurs freely as well as in combined form in the nature. It is present in sweet fruits and honey. It is also present in large quantities in ripe grapes. It is also known as grape sugar or dextrose.

Preparation of Glucose

(i) **From Sucrose** (Cane sugar) Glucose can be easily obtained in a laboratory by the hydrolysis of alcoholic solution of cane sugar, i.e. sucrose with dilute HCl or H_2SO_4 at 50°C to give glucose and fructose in equal amounts.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(ii) **From Starch** On large scale, glucose is obtained by the hydrolysis of starch by boiling it with hot dilute H_2SO_4 at 393 K, under 2-3 standard atmospheric pressure.

$$\underset{\text{Starch or Cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[393\,K;\ 2\text{-}3\ atm]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Structure of Glucose

As glucose is an aldohexose, it consists of six C-atoms and an aldehyde group. It is the monomer of many of the larger carbohydrates such as starch, cellulose, etc. It is the most abundant organic compound on the earth and used as an immediate source of energy for all metabolic reactions in the animals.

Structural Evidences for Glucose

Glucose was assigned the following structure on the basis of the evidences mentioned below :

$$\begin{array}{ll} \text{CHO} & \longleftarrow \text{Aldehydic group} \\ | & \\ (\text{CHOH})_4 & \longleftarrow \text{Four 2° alcoholic groups} \\ | & \\ \text{CH}_2\text{OH} & \longleftarrow \text{1° alcoholic group} \end{array}$$

Glucose

(i) **Molecular Formula** The molecular formula of glucose was found to be $C_6H_{12}O_6$.

(ii) **Presence of Straight Chain (Reaction with HI)** When heated with HI for a long time, it forms *n*-hexane which shows that all six carbon atoms are linked in a straight chain.

$$\underset{\text{Glucose}}{CHO-(CHOH)_4-CH_2OH} \xrightarrow{HI,\ \Delta} \underset{n\text{-hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3}$$

(iii) **Presence of Carbonyl Group ($\rangle C{=}O$)**

Glucose reacts with hydroxylamine to form an oxime and adds a molecule of hydrogen cyanide to give cyanohydrin.

$$CHO-(CHOH)_4-CH_2OH \xrightarrow[-H_2O]{NH_2OH} \underset{\text{Glucose oxime}}{CH{=}N{-}OH-(CHOH)_4-CH_2OH}$$

$$CHO-(CHOH)_4-CH_2OH \xrightarrow{HCN} \underset{\text{Glucose cyanohydrin}}{CH(CN)(OH)-(CHOH)_4-CH_2OH}$$

(iv) **Presence of an Aldehydic Group (Oxidation)** On reaction with a mild oxidising agent like bromine water, Tollen's reagent or Fehling's solution, glucose gets oxidised to six carbon carboxylic acid (gluconic acid).

$$CHO-(CHOH)_4-CH_2OH \xrightarrow[\text{(Oxidation)}]{Br_2\ \text{water}} \underset{\text{Gluconic acid}}{COOH-(CHOH)_4-CH_2OH}$$

(v) **Presence of Five —OH Groups Linked to Different Carbon Atoms** Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five —OH groups.

$$\underset{\text{Glucose}}{CHO-(CHOH)_4-CH_2OH} \xrightarrow[\text{(Acetylation)}]{5\,(CH_3CO)_2O\ \text{(Acetic anhydride)}} \underset{\substack{\text{Glucose pentaacetate}\\ \text{(Stable compound)}}}{CHO-(CH-O-\overset{O}{\overset{\|}{C}}-CH_3)_4-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3} + 5CH_3COOH$$

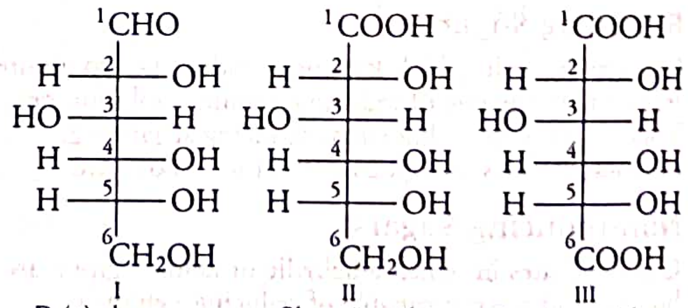
Since, the presence of two or more OH groups on the same carbon atom makes the molecule unstable but as glucose exists as a stable compound, this suggests that five —OH groups should be attached to different carbon atoms.

(vi) **Presence of One Primary Alcoholic Group** On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, called saccharic acid. This indicates the presence of one primary alcoholic (—OH) group in glucose.

$$\underset{\text{Glucose}}{CHO-(CHOH)_4-CH_2OH} \xrightarrow[HNO_3]{\text{(Oxidation)}} \underset{\text{Saccharic acid}}{COOH-(CHOH)_4-COOH} \xleftarrow[HNO_3]{\text{Oxidation}} \underset{\text{Gluconic acid}}{COOH-(CHOH)_4-CH_2OH}$$

Configuration of Glucose

Emil Fischer gave the exact spatial arrangement of different —OH groups in glucose after studying many other properties. Its configuration is correctly represented as I. So, gluconic acid is represented as II and saccharic acid as III.



I D-(+)-glucose   II Gluconic acid   III Saccharic acid

Glucose is named as D-(+)-glucose in which 'D' represents the configuration whereas '(+)' represents the dextrorotatory nature of the molecule.

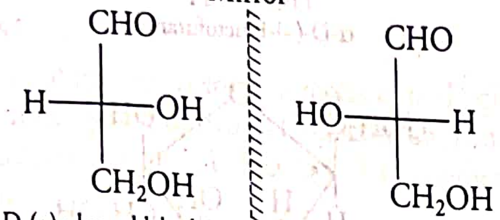
Note D and L has no relation with the optical activity of the compound.

D and L-Notations

D and L before the name of any compound commonly indicate the relative configuration of a particular stereoisomer,

e.g. glyceraldehyde contains one asymmetric carbon atom and exists in two enantiomeric forms as given below:

Mirror

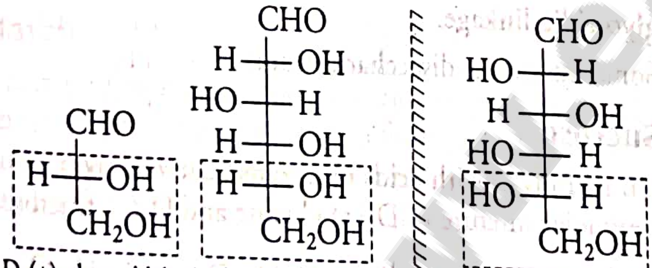


D-(+)-glyceraldehyde L-(–)-glyceraldehyde

Compounds which can be chemically correlated to (+)-isomer of glyceraldehyde are said to have D-configuration whereas those which can be correlated to (–)-isomer of glyceraldehyde are said to have L-configuration.

For assigning the configuration of monosaccharides, it is the lowest asymmetric carbon atom (as shown below) which is compared, e.g. in (+)-glucose, —OH on the lowest asymmetric carbon is on the right side which is comparable to (+)-glyceraldehyde. Thus, it is assigned as D-configuration.

Mirror



D-(+)-glyceraldehyde D-(+)-glucose L-(–)-glucose

Cyclic Structure of Glucose

The linear structure of glucose explained most of its properties but failed to explain the following facts and reactions:

(i) Even though an aldehyde group is present, the glucose does not react with NH_3, 2, 4-DNP and Grignard reagent.

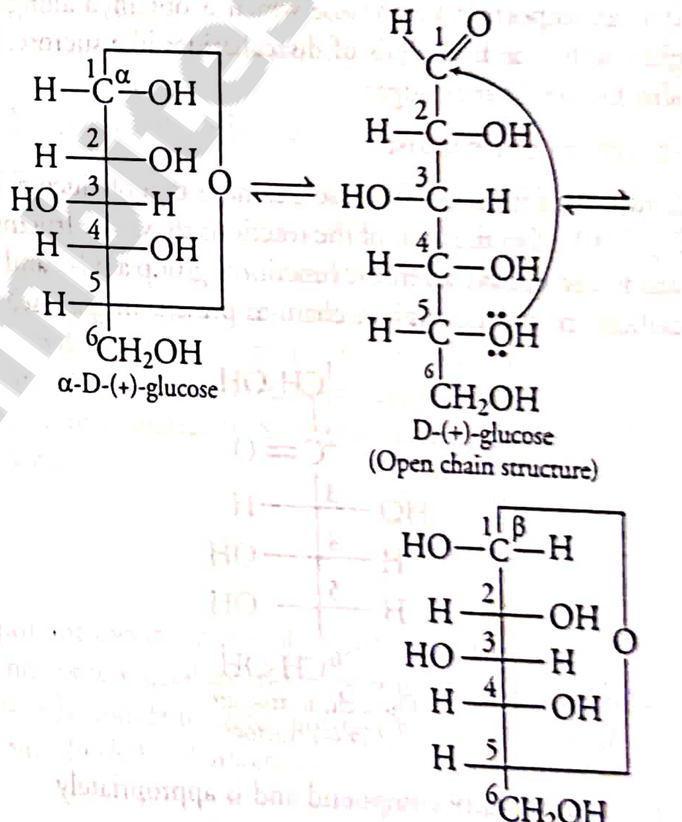
(ii) Glucose do not restore the pink colour of Schiff 's reagent, despite having an aldehydic group.

(iii) The pentaacetate of glucose does not react with hydroxylamine which shows the absence of free —CHO group.

(iv) Glucose exists in two different crystalline forms which are named as α and β. The α-form of glucose (mp 419 K) is obtained by crystallisation from concentrated solution of glucose at 303 K, while the β-form (mp 423 K) is obtained by crystallisation from hot and saturated aqueous solution at 371 K.

This behaviour could not be explained by the open chain structure of glucose. It was suggested that one of the —OH groups may add to the —CHO group and form a cyclic hemiacetal structure.

It was found that glucose forms a six membered ring in which —OH at C-5 is involved in the ring formation. This explains the absence of —CHO group and existence of glucose in two forms as shown below:



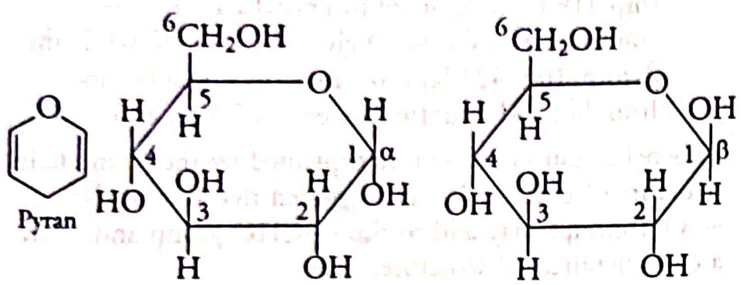
α-D-(+)-glucose D-(+)-glucose (Open chain structure) β-D-(+)-glucose

Fischer projection formulae

The two cyclic forms (α - and β-forms) exist in equilibrium with open chain structure.The above two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C - 1 atom. This C - 1 atom is called anomeric carbon, i.e. the aldehydic carbon before cyclisation. Such isomers i.e. α- form and β -form differ in configuration only around C_1 are called **anomers.**

Pyranose structure The six membered cyclic structure of glucose is known as pyranose structure (α- or β-). It is analogous to pyran which is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring.

The cyclic structure of glucose is more correctly represented by Haworth structures as given below :



α-D-(+)-glucopyranose β-D-(+)-glucopyranose

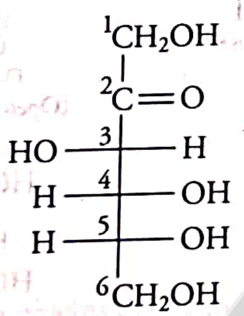
Haworth structures

Fructose

It is an important ketohexose which is obtained along with glucose by the hydrolysis of disaccharides like sucrose. It is also known as fruit sugar.

Structure of Fructose

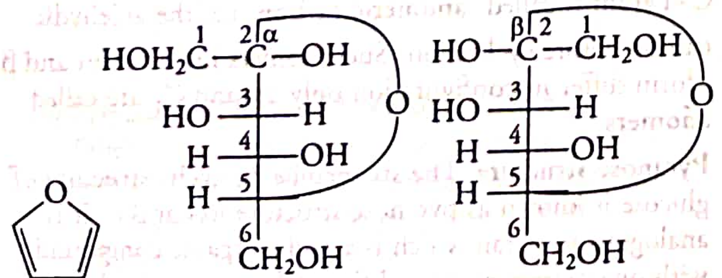
Molecular formula of fructose is same as that of glucose, i.e. $C_6H_{12}O_6$. On the basis of the reactions shown by fructose, it was found to have a ketonic functional group at C-2 and six carbon atoms in a straight chain as present in glucose.



Open chain structure of D-(−)-fructose

It is a laevorotatory compound and is appropriately written as D-(−)-fructose.

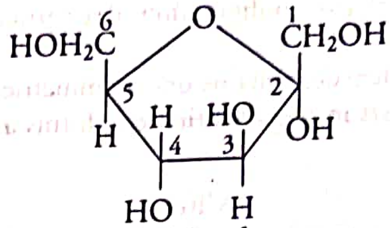
It also exists in two cyclic forms which are obtained by the addition of —OH at C-5 to the ($>$C=O) group. The ring thus formed is a five membered ring named as furanose analogous to furan, which is a five membered cyclic compound with one oxygen and four carbon atoms.



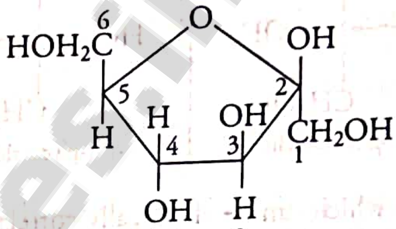
Furan α-D-(−)-fructofuranose β-D-(−)-fructofuranose

Fischer projection formulae

The cyclic structures of two anomers of fructose are represented by Haworth structures as given below:



α-D-(−)-Fructofuranose



β-D-(−)-Fructofuranose

Haworth structures

Disaccharides

Disaccharides on hydrolysis with dilute acids or enzymes give two molecules of monosaccharides. These molecules may be either same or different monosaccharides.

The two monosaccharide units are joined together through an oxide linkage which is formed by the loss of a water molecule. Such a linkage between two monosaccharide units through an oxygen atom is called **glycosidic linkage**.

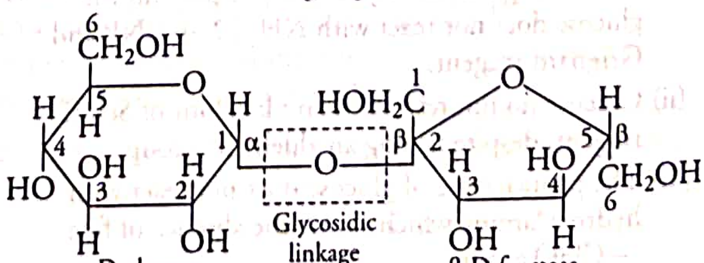
Some important disaccharides are:

Sucrose

On hydrolysis with acids or enzyme, sucrose gives equimolar mixture of D-(+)-glucose and D-(−)-fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{HCl} \underset{\text{D-(+)-glucose}}{C_6H_{12}O_6} + \underset{\text{D-(−)-fructose}}{C_6H_{12}O_6}$$

These two monosaccharides are linked through a glycosidic linkage between C-1 of α-glucose and C-2 of β-fructose. Since, the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar.



α-D-glucose Glycosidic linkage β-D-fructose

Haworth structure of sucrose

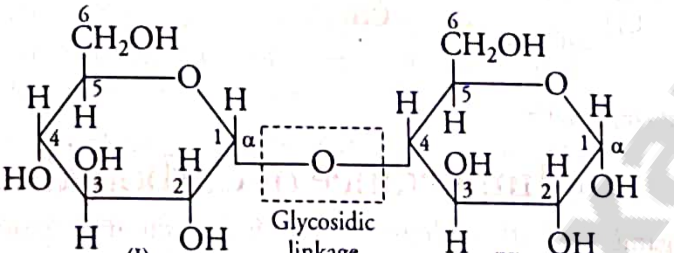
Although, sucrose is dextrorotatory but after hydrolysis, it gives dextrorotatory glucose and laevorotatory fructose. The mixture is laevorotatory because laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+52.5°).

Therefore, hydrolysis of sucrose brings about a change in the sign of rotation, i.e. form dextro (+) to laevo (–) and hence, the product is known as **invert sugar.** This over all process is called **inversion of sugar.**

Maltose

Hydrolysis of maltose yields two moles of α -D-glucose. Thus, it is composed of two α-D-glucose units in which C-1 of one glucose unit (I) is linked to C-4 of another glucose unit (II).

The free aldehyde group can be produced at C-1 of second glucose in solution and it shows reducing properties. So, it is a reducing sugar.

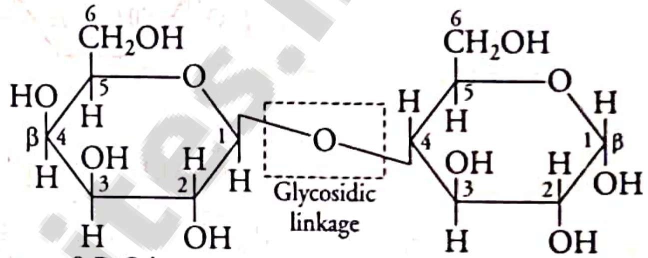


(I) α-D-Glucose (II) α-D-Glucose

Haworth structure of maltose

Lactose

It is commonly known as milk sugar because it is found in milk. It is composed of β-D-galactose and β-D-glucose. The linkage is between C-1 of galactose and C - 4 of glucose. Since, it reduces Tollen's or Fehling's solution, Hence, it is also called a **reducing sugar.**



β-D-Galactose β-D-Glucose

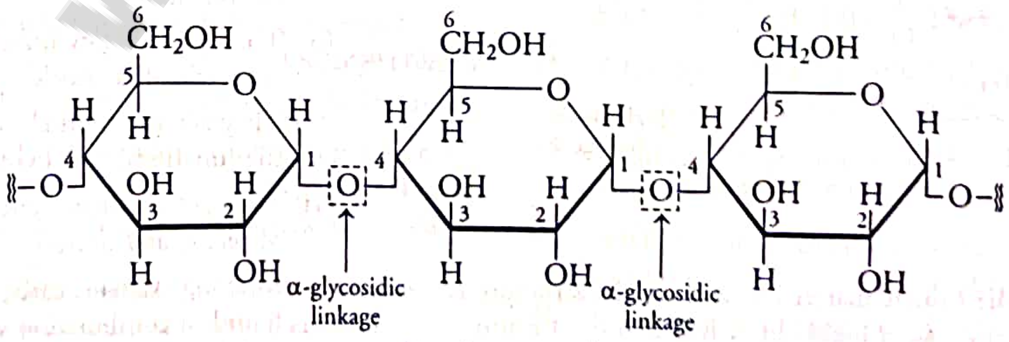
Haworth structure of lactose

Polysaccharides

These are the most commonly found carbohydrates in nature. They are composed of a large number of monosaccharide units joined together by glycosidic linkages. These are colourless, tasteless, amorphous powders. They play a vital role in plant and animal life, by acting as the food storage material or structural materials. Some important polysaccharides are :

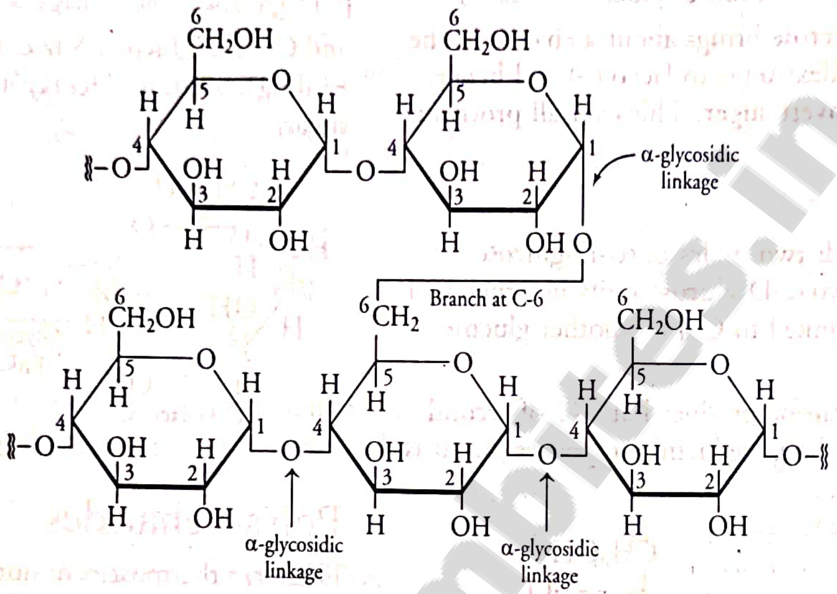
Starch

It is important storage polysaccharide of plants and the most important dietary source of carbohydrate for human beings. High content of starch is found in cereals, roots, tubers and some vegetables. It is a polymer of α-glucose and consists of two components, i.e. **amylose** and **amylopectin.** Amylose is soluble in water and constitutes 15-20% of starch while amylopectin is insoluble in water and constitutes about 80 - 85% of starch.



Structure of amylose

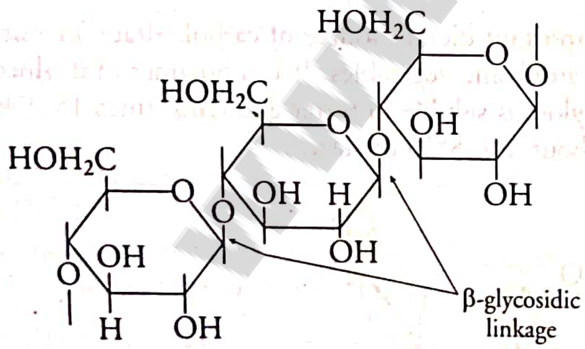
Chemically, amylose is a long unbranched chain with 200-1000 α-D(+)-glucose units that are held together by C_1-C_4 glycosidic linkage. On the other hand, amylopectin is a highly branched chain polymer of α-D-glucose units in which glycosidic linkage is present between C_1-C_4 atoms, whereas the branching occurs through C_1-C_6 glycosidic linkage.



Structure of amylopectin

Cellulose

It occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is the main constituent of cell wall of plant cells. It is a straight chain polysaccharide composed only of β-D-glucose units that are linked together by glycosidic linkage between C-1 of one glucose unit and C-4 of the next glucose unit.



Structure of cellulose

Glycogen

It is known to be the storage material of animals. Its structure is similar to amylopectin and is highly branched that is why also known as animal starch. It is found in liver, muscles and brain.

When body requires energy, it breaks down to glucose by the action of enzymes. It is also found in yeast and fungi.

Importance of Carbohydrates

Carbohydrates are very important and essential for life in both plants and animals.

Few important roles of carbohydrates are listed below :

(i) They form a major portion of our food.

(ii) They are used as storage materials like starch in plants and glycogen in animals.

(iii) Cellulose in the form of wood is used to build furniture and clothes in the form of cotton fibres.

(iv) They provide raw materials for many industries, like textiles, papers and lacquers.

(v) They act as a biofuel to provide energy for the functioning of living organisms.

(vi) They act as constituent of cell membranes of plants and bacteria.

(vii) In living systems, carbohydrates are also found in combination with many proteins and lipids such as glycoproteins and glycolipids.

TOPIC PRACTICE 1

OBJECTIVE Type Questions

1. Carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone is called
   (a) monosaccharide (b) oligosaccharide
   (c) polysaccharide (d) None of these

2. α-D-glucose and β-D-glucose differ from each other with respect to the **CBSE SQP (Term I)**
   (a) number of – OH groups
   (b) configuration at the C-1 carbon
   (c) size of the hemiacetal ring
   (d) configuration at the C-5 carbon

3. One molecule of sucrose on hydrolysis gives .... **NCERT Exemplar**
   (a) 2 molecules of glucose
   (b) 2 molecules of glucose + 1 molecule of fructose
   (c) 1 molecule of glucose +1 molecule of fructose
   (d) 2 molecules of fructose

4. Disaccharides that are reducing in nature are **CBSE SQP 2021**
   (a) sucrose and lactose
   (b) sucrose and maltose
   (c) lactose and maltose
   (d) sucrose, lactose and maltose

5. Which one of the following reactions is not explained by the open chain structure of glucose? **CBSE SQP (Term I)**
   (a) Formation of penta-acetate of glucose with acetic anhydride
   (b) Formation of addition product with 2,4-DNP reagent
   (c) Silver mirror formation with Tollen's reagent
   (d) Existence of alpha and beta forms of glucose

6. Which of the following is a polysaccharide? **CBSE SQP (Term I)**
   (a) Glucose (b) Maltose (c) Glycogen (d) Lactose

7. Which one of the following statement is correct about sucrose? **CBSE SQP (Term I)**
   (a) It can reduce Tollen's reagent however cannot reduce Fehling's reagent
   (b) It undergoes mutarotation like glucose and fructose
   (c) It undergoes inversion in the configuration on hydrolysis
   (d) It is laevorotatory in nature

8. In the following reaction, identify A and B

$$\begin{array}{l} C_6H_{12}O_6 \xrightarrow{\text{Acetic anhydride}} A \\ \quad \big\downarrow \text{Conc. nitric acid} \\ \quad B \end{array}$$

CBSE SQP (Term I)

   (a) $A = COOH—(CH_2)_4—COOH$,
   $B = OHC—(CHOCOCH_3)_4—CH_2OCOCH_3$
   (b) $A = COOH—(CH_2)_4—CHO$,
   $B = OHC—(CHOCOCH_3)_4—CH_2OCOCH_3$
   (c) $A = OHC—(CHOCOCH_3)_3—CH_2OCOCH_3$,
   $B = COOH—(CH_2)_4—CHO$
   (d) $A = OHC—(CHOCOCH_3)_4—CH_2OCOCH_3$,
   $B = COOH—(CH_2)_4—COOH$

VERY SHORT ANSWER Type Questions

9. Classify the following into monosaccharides and disaccharides. Ribose, 2-deoxyribose, maltose, galactose, fructose and lactose. **NCERT**

10. Which one of the following is a disaccharide? starch, maltose, fructose, glucose **Delhi 2015**

11. Which one of the following is a polysaccharide? starch, maltose, fructose, glucose **Delhi 2020, All India 2015**

12. What are reducing sugars? **All India 2010; NCERT**

13. Glucose on reaction with HI gives n-hexane. What does it suggest about the structure of glucose? **All India 2014**

Or Write the product formed when glucose is treated with HI.

14. Write the product formed on reaction of D-glucose with Br_2 water. **All India 2014**

15. Define the term anomers. **Delhi 2014**

16. What do you understand by the term glycosidic linkage? **NCERT; Delhi 2013, All India 2011 C**

17. What are the products of hydrolysis of sucrose? **All India 2014; Delhi 2014, 2013; NCERT**

18. What are the products of hydrolysis of maltose? **Delhi 2014, 2013**

19. What are the expected products of hydrolysis of lactose?. **Delhi 2014; NCERT Intext**

20. Name the two components of starch. **Delhi 2013**

21. Which of the two components of starch are water soluble ? **All India 2014, 2013**

22. Which component of starch is a branched polymer of α-glucose and insoluble in water? **All India 2014**

23. Write the two main functions of carbohydrate in plants. **All India 2008; NCERT**

SHORT ANSWER Type I Questions

24. Why are carbohydrate generally optically active?
25. Write the reactions involved when D-glucose is treated with the following reagents :
(i) HCN (ii) Br_2 water **All India 2013**
26. Why does the mixture obtained after hydrolysis of cane sugar is laevorotatory though sugar itself is dextrorotatory?
27. Name the two components of starch. How do they differ from each other structurally?
28. What is the essential difference between the α-form of glucose and β-form of glucose? Explain.
29. Monosaccharides contain carbonyl group hence are classified, as aldose or ketose. The number of carbon atoms present in the monosaccharide molecule are also considered for classification. In which class of monosaccharide will you place fructose? **NCERT Exemplar**
30. Carbohydrates are essential for life in both plants and animals. Name the carbohydrates that are used as storage molecules in plants and animals. Also, name the carbohydrate which is present in wood or in the fibre of cotton cloth. **NCERT Exemplar**

SHORT ANSWER Type II Questions

31. What happens when D-glucose is treated with the following reagents? **NCERT**
(i) HI (ii) Br_2 water (iii) HNO_3
32. How will you distinguish 1° and 2° hydroxyl groups present in glucose ? Explain with reactions. **NCERT Exemplar**
33. Enumerate the reaction of D-glucose which cannot be explained by the open chain structure. **Delhi 2014 C, 2011C; All India 2009; NCERT**

Or Which type of reactions could not be explained by the open chain structure of glucose? What alternative structure has been proposed for the glucose molecule? Draw the structure.
34. Define the following terms.
(i) Glycosidic linkage (ii) Invert sugar
(iii) Oligosaccharides **Delhi 2014**
35. What is glycogen? How is it different from starch? **NCERT**
36. What is the basic structural difference between starch and cellulose? **NCERT**

HINTS AND EXPLANATIONS

1. (*a*) A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone is called monosaccharide.
2. (*b*) α-D-glucose and β-D-glucose differ from each other with respect to the configuration at the C–1 carbon.
3. (*c*) Sucrose (cane sugar) is a disaccharide. One molecule of sucrose on hydrolysis gives one molecule of glucose and one molecule of fructose.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} \xrightarrow[H^+]{H_2O} \underset{D(+)\text{ glucose}}{C_6H_{12}O_6} + \underset{D(-)\text{ fructose}}{C_6H_{12}O_6}$$

4. (*c*) Lactose and maltose.
5. (*d*) Existence of alpha and beta forms of glucose is not explained by the open chain structure of glucose.
6. (*c*) Glycogen
7. (*c*) Sucrose undergoes inversion in the configuration.
8. (*c*) Refer to text on page 408.
9. **Monosaccharides** Ribose, 2-deoxyribose, galactose, and fructose. **Disaccharides** Maltose and lactose.
10. Maltose is a disaccharide. It is composed of two α-D-glucose molecules.
11. Starch is a polysaccharide. It gives the large number α-D-glucose molecules on hydrolysis.
12. Carbohydrates in which ketonic or aldehydic groups are free and capable of reducing Fehling's solution or Tollen's reagent are known as reducing sugars.
13. This reaction shows that all six carbon atoms are linked in a straight chain.
14.

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{Br_2\ \text{water}} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

15. A pair of isomers that differ in configuration around C-1 atom are called anomers.
16. A linkage between two monosaccharide units through an oxygen atom is called glycosidic linkage.
17. The products obtained on hydrolysis of sucrose are D-(+)-glucose and D-(–)-fructose.

18. Maltose gives two molecules of D-glucose on hydrolysis.

19. Lactose on hydrolysis gives β-D-glucose and β-D-galactose.

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

20. Starch is composed of amylose and amylopectin.

21. Starch consists of amylose and amylopectin. Amylose is a water soluble component of starch.

22. Amylopectin is a branched polymer of α-glucose and insoluble in water.

23. (i) Carbohydrates are used as storage molecules as starch in plants.
    (ii) Cell wall of bacteria and plants is made up of cellulose.

24. Hint Chiral carbon atoms.

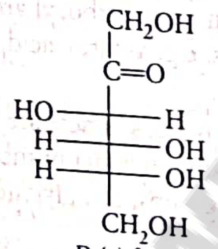
25. Refer to text on page 408.

26. After hydrolysis, cane sugar (sucrose) gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (−92.4°) is more than dextrorotation of glucose (+52.5°), the mixture is laevorotatory.

27. Refer to text on pages 411 and 412.

28. Refer to text on page 409.

29. Monosaccharides contain carbonyl group. Hence, are classified as aldose or ketose.When aldehyde group is present, the monosaccharides are known as aldose. When ketone group is present, the monosaccharides are known as ketose. Fructose has molecular formula $C_6H_{12}O_6$ containing six carbon and keto group. It is classified as ketohexose.



D-(−)-fructose

30. In plants, carbohydrates are stored in the form of starch while in animals, these are stored in the form of glycogen.
Cellulose, a carbohydrate is present in wood or in the fibre of cotton cloth.

31. Refer to text on page 408.

32. Glucose consists of 5 —OH groups. Among these, the —OH group present on the terminal carbon atom (i.e. C-6 atom) is called 1° hydroxyl group while all the four remaining —OH groups present on C-2, C-3, C-4 and C-5 atoms are called 2° hydroxyl groups. 1° hydroxyl groups are easily oxidised to carboxylic acid group while 2° hydroxyl groups undergo oxidation only under drastic conditions.
e.g. On oxidation with nitric acid, glucose gives a dicarboxylic acid, saccharic acid (also called glycaric acid) having the same number of carbon atoms as glucose. This indicates that glucose contains one primary (1°) alcoholic or hydroxyl group.

$$\underset{\text{Glucose}}{\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}} \xrightarrow[\text{Oxidation}]{HNO_3} \underset{\text{Saccharic acid}}{\begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ COOH \end{array}}$$

33. Refer to text on page 409.

34. (i) Refer to text on page 410.
    (ii) The equimolar mixture of D-(+)-glucose and D-(−)-fructose which sucrose gives on hydrolysis is called invert sugar.
    (iii) Refer to text on page 407.

35. Glycogen is a highly branched condensation polymer of α-D-glucose. It is stored in the form of glucose in liver and muscles of human beings. In contrast, starch is a chief storage polysaccharide of plants and consists of a mixture of two components, amylose (water soluble component 15-20%) and amylopectin (water insoluble component 80-85%). Amylose is a linear polymer of α-D-glucose, while amylopectin is a highly branched polymer of α-D-glucose.
Thus, both glycogen and amylopectin are branched chain condensation polymer of α-D-glucose. The only difference is that amylopectin chain consists of 20-25 glucose units whereas glycogen chain consists of 10-14 glucose units.

36. Refer to text on pages 411 and 412.

|TOPIC 2|

Proteins and Enzymes

Another class of biomolecules which are essential for living systems, are proteins. Proteins are the most abundant biomolecules of the living system. The chief sources of proteins are milk, cheese, pulses, fish, meat, peanuts, etc. They are found in every part of the body and form a fundamental basis of structure and functions of life. These are also required for growth and maintenance of body. The word protein is derived from Greek word, '*proteios*' meaning 'primary' or 'of prime importance'. Chemically, proteins are the polymers in which the monomeric units are the α-amino acids.

AMINO ACIDS

Amino acids contain amino (—NH_2) and carboxyl (—COOH) functional groups.

Depending upon the relative position of amino group with respect to carboxyl group, the amino acids can be classified as α, β, γ or δ.

$$\underset{\substack{\text{NH}_2 \longleftarrow \alpha\text{-amino group}}}{R-\overset{\alpha}{\text{CH}}-\text{COOH}} \longleftarrow \text{Carboxylic group}$$

α-amino acid
(R = side chain)

On hydrolysis of proteins, only α-amino acids are obtained.

$$\text{Proteins} \xrightarrow{\text{Hydrolysis}} \text{Peptides} \xrightarrow{\text{Hydrolysis}} \alpha\text{-amino acids}$$

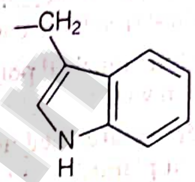
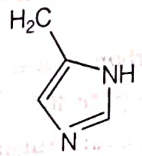
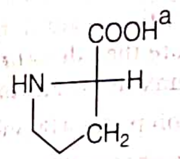
Nomenclature of Amino Acids

Amino acids can be named by the IUPAC system, but they are generally known by their trivial names depending upon the source from which they are obtained or the property of that compound etc.

e.g. Glycine is named due to its sweet taste (in Greek '*glykos*' means sweet) and tyrosine was first obtained from cheese (in Greek, *tyros* means 'cheese'). Amino acids are represented by three letters symbol, which is first three letters of their respective common names.

The structures of some commonly occurring amino acids along with their symbols can be summarised as follows:

Natural amino acids

Name of the amino acids	Characteristic feature of side chain, R	Three letters symbol	One letter code
Glycine	H	Gly	G
Alanine	$-CH_3$	Ala	A
Valine*	$(H_3C)_2CH-$	Val	V
Leucine*	$(H_3C)_2CH-CH_2-$	Leu	L
Isoleucine*	$H_3C-CH_2-(CH_3)-CH-$	Ile	I
Arginine*	$HN{=}\underset{\substack{\vert \\ NH_2}}{C}-NH(CH_2)_3-$	Arg	R
Lysine*	$H_2N-(CH_2)_4-$	Lys	K
Glutamic acid	$HOOC-CH_2-CH_2-$	Glu	E
Aspartic acid	$HOOC-CH_2-$	Asp	D
Glutamine	$H_2N-CO-CH_2-CH_2-$	Gln	Q
Asparagine	$H_2N-CO-CH_2-$	Asn	N
Threonine*	$H_3C-CHOH-$	Thr	T
Serine	$HO-CH_2-$	Ser	S
Cysteine	$HS-CH_2-$	Cys	C
Methionine*	$H_3C-S-CH_2-CH_2-$	Met	M
Phenylalanine*	$C_6H_5-CH_2-$	Phe	F
Tyrosine	$(p)\ HO-C_6H_4-CH_2-$	Tyr	Y
Tryptophan*		Trp	W
Histidine*		His	H
Proline		Pro	P

*Essential amino acids, a = Complete structure

Classification of Amino Acids

Depending upon the relative number of amino and carboxyl groups present in their molecule, amino acids are classified as:

(i) **Acidic amino acids** These are the amino acids which contain more carboxyl group than amino groups, e.g. aspartic acid, glutamic acid, etc.

(ii) **Neutral amino acids** These are the amino acids which contain equal number of amino and carboxyl groups, e.g. glycine, alanine, etc.

(iii) **Basic amino acids** These are the amino acids which contain more number of amino groups than carboxyl groups, e.g. lycine, arginine, etc.

ESSENTIAL AND NON-ESSENTIAL AMINO ACIDS

Amino acids which are synthesised by the body, are called non-essential. On the other hand, those amino acids which cannot be synthesised in the human body and are supplied in the form of diet (because they are required for proper health and growth) are called essential amino acids. The ten essential amino acids are marked by asterisks * in the above table.

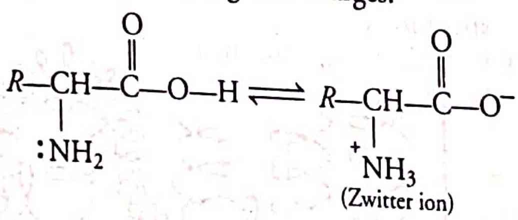
Properties of Amino Acids

Some of the important properties of amino acids are:

(i) Amino acids are usually colourless, crystalline solids. These are soluble in water and have high melting points.

(ii) Amino acids contain both acidic (carboxyl group) and basic (amino group) groups due to which they behave like salts rather than simple amines.

(iii) In aqueous solution, they neutralise each other involving transfer of a proton from the carboxyl group to the amino group, giving rise to a dipolar ion known as '**Zwitter ion**'. It is neutral but contains both positive and negative charges.



In Zwitter ionic form, amino acids show amphoteric behaviour as they can react with both acids and bases.

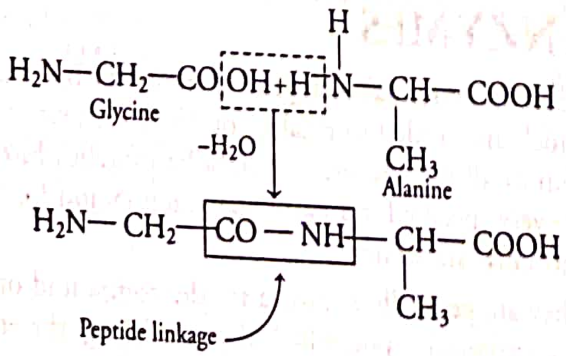
(iv) Except glycine, all other α-amino acids are optically active as their α-carbon is asymmetric. These exist in both 'D' and 'L' forms. Most of the amino acids have L-configuration in which $-NH_2$ group is on left hand side.

Peptide Linkage and Their Classification

Proteins are connected to each other by $-CO-NH-$ bond which is called the **peptide bond** or the peptide linkage. Chemically, peptide linkage is an amide ($-CO-NH-$) bond formed between carboxyl group ($-COOH$) and amino group ($-NH_2$).

The reaction between two molecules of similar or different amino acids, proceed through the combination of the amino group of one molecule with the carboxyl group of the other, resulting in the elimination of a water molecule and formation of a peptide bond ($-CONH-$). The product of the reaction is called **dipeptide** because it is made up of two amino acids.

e.g. Glycylalanine is formed when carboxyl group of glycine combines with the amino group of alanine.



If a third amino acid combines to a dipeptide, the product is called a **tripeptide**. A tripeptide contains three amino acids linked by two peptide linkages. Thus, according to the number of amino acids combined, the product may be tetrapeptide, pentapeptide or hexapeptide. When the number of such amino acids is more than ten, then the products are called **polypeptides**. A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000 u, is called a **protein**.

However, the distinction between a polypeptide and a protein is not very sharp. Polypeptides with fewer amino acids are likely to be called proteins if they ordinarily have a well defined conformation of protein such as insulin which contains only 51 amino acids.

Classification of Proteins

On the basis of their molecular shape, proteins are of two types:

(i) **Fibrous proteins** They have thread or fibre like structures in which polypeptide chains run parallel and are held together by hydrogen and disulphide bonds. These proteins are insoluble in water, e.g. keratin (found in hair, skin, nails, wool, silk) and myosin (present in muscles).

(ii) **Globular proteins** They have spherical shape structure which results when the chains of polypeptides coil around. These are soluble in water, e.g. insulin and albumins.

Structure and Shape of Proteins

On the basis of structure and shape of proteins, four different levels are found:

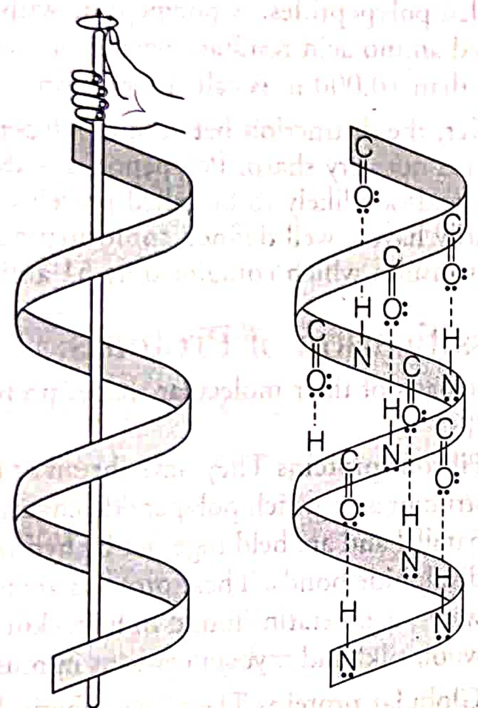
(i) **Primary structure** Proteins may have one or more polypeptide chains. Each polypeptide chain has a large number of α-amino acids linked to one another in a specific sequence. The specific sequence in which various amino acids are linked with each other to form a polypeptide, is called its primary structure.

So, the change of just one amino acid in the sequence can alter its biological activity and can create a different protein.

(ii) **Secondary structure** The conformation which the polypeptide chains assume as a result of hydrogen bonding between $-\overset{\overset{\displaystyle O}{\|}}{C}-$ and $-NH-$ groups of the peptide bond is called secondary structure of proteins.

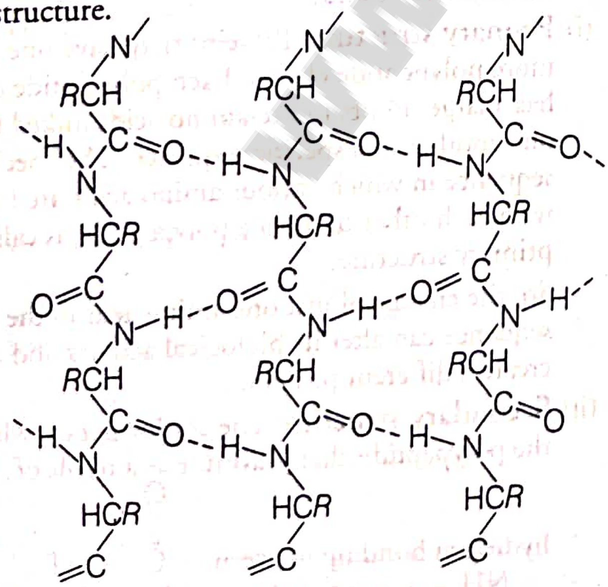
They exist in two different structures which are as follows :

(a) **α-helix structure** It is one of the most common structure in which a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed helix. In this structure, the —NH group of each amino acid unit is hydrogen bonded to the C=O of another amino acid unit present at an adjacent turn of the helix.



α-helix structure of proteins

(b) **β-pleated sheet structure** All peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds. The structure so formed resembles the pleated folds of drapery and thus, it is known as β-pleated sheet structure.

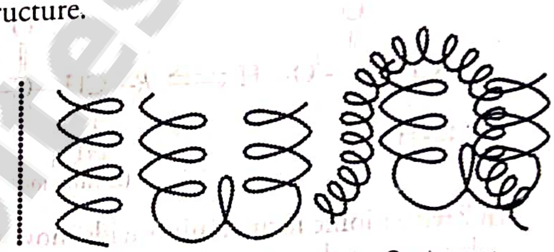


β-pleated sheet structure of proteins

(iii) **Tertiary structure** The further folding of the secondary structure of proteins is known as tertiary structure. It gives rise to two major molecular shapes, fibrous and globular. The main forces that stabilise 2° and 3° structures of protein are hydrogen bonds, disulphide bonds, van der Waals' forces and electrostatic forces of attraction.

(iv) **Quaternary structure** Although many proteins exist as a single polypeptide chain, but some of the proteins are composed of two or more polypeptide chains called subunits.

The spatial arrangement of these subunits with respect to each other is known as quaternary structure.



Diagrammatic representation of protein structure (two subunits of two types in quaternary structure)

Denaturation of Proteins

Protein found in a biological system with a unique three-dimensional structure and biological activity, is called native protein. When a native protein is subjected to physical change (like change in temperature) or chemical change (like change in pH), the hydrogen bonds are disturbed.

As a result, globules unfold and helix get uncoiled and protein loses its biological activity. This is known as denaturation of protein. During denaturation, 2° and 3° structures are destroyed but 1° structure remains intact, e.g. coagulation of an egg white on boiling and curdling of milk caused due to the formation of lactic acid by the bacteria present in milk.

ENZYMES

These are essential biological catalysts (or biocatalysts) which are needed to catalyse biochemical reactions. Almost all the enzymes are globular proteins. Enzymes are very specific for a particular reaction and for a particular substrate.

They are generally named after the compound or class of compounds upon which they work, e.g. the enzyme

that catalyses hydrolysis of maltose into glucose is named as maltase.

e.g.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow[H_2O]{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

Sometime enzymes are also named after the reaction, where they are used. The enzyme which catalyses the oxidation of one substrate with simultaneous reduction of another substrate are named as oxidoreductase enzymes. The ending of the name of an enzyme is '-ase'.

Mechanism of Enzyme Action

Enzymes are needed only in small quantities for the progress of a reaction. Like chemical catalysts, enzyme reduces the magnitude of activation energy, e.g. activation energy for acid hydrolysis of sucrose is 6.22 kJ mol^{-1}, while the activation energy is only 2.15 kJ mol^{-1}, when hydrolysed by the enzyme, sucrase.

Note Mechanism for the enzyme action has been discussed in chapter 5.

TOPIC PRACTICE 2

OBJECTIVE Type Questions

1. An α-helix is a structural feature of **All India 2020**
(a) sucrose (b) polypeptides
(c) nucleotides (d) starch

2. Which one of the following amino acid has phenyl —OH group?
(a) Lysine (b) Arginine
(c) Proline (d) Tyrosine

3. Which of the following amino acids is not optically active?
(a) Lysine (b) Glycine
(c) Leucine (d) Glutamine

4. The functional unit that is repeated in a protein molecule is **CBSE SQP (Term I)**
(a) an ester linkage
(b) a glycosidic linkage
(c) a peptide linkage
(d) an ether linkage

5. *Which of the following statement is correct?* **CBSE SQP (Term I)**
(a) *Fibrous proteins are generally soluble in water*
(b) *Albumin is an example of fibrous proteins*
(c) *In fibrous proteins, the structure is stabilised by hydrogen bonds and disulphide bonds*
(d) *pH does not affect the primary structure of protein*

6. Tertiary structure of protein is stabilised by **NCERT Exemplar**
(a) disulphide bonds
(b) van der Waals' forces
(c) hydrogen bonds
(d) All of the above

7. Curdling of milk is an example of **CBSE Sample paper**
(a) breaking of peptide linkage
(b) hydrolysis of lactose
(c) breaking of protein into amino acids
(d) denaturation of proetin

8. Enzymes are
(a) oils (b) fatty acids
(c) proteins (d) minerals

VERY SHORT ANSWER Type Questions

9. Amino acids can be classified as α, β, γ, δ and so on depending upon the relative position of amino group with respect to carboxyl group. Which type of amino acids forms polypeptide chain in proteins? **NCERT Exemplar**

10. Amino acids show amphoteric behaviour. Why? **All India 2015**

11. What type of linkage is responsible for the formation of proteins? **All India 2014**

Or Write the name of linkage joining two amino acids. **All India 2013**

12. Three amino acids are given below:
Alanine $CH_3CH(COOH)(NH_2)$, aspartic acid $HOOC-CH_2CH(COOH)(NH_2)$ and lysine $H_2N-(CH_2)_4-CH(COOH)(NH_2)$ **CBSE SQP 2021**
(i) Make two tripeptides using these amino acids and mark the peptide linkage in both cases.
(ii) Represent alanine in the Zwitter ionic form.

13. What is the difference between fibrous protein and globular protein? **Delhi 2020, NCERT, Delhi 2015**

14. Give an example for each of fibrous protein and globular protein. **All India 2014**

15. Write one difference between α-helix and β-pleated sheet structures of protein **All India 2015**

16. What type of bonding helps in stabilising the α-helix structure of proteins? **NCERT; All India 2010 C; Delhi 2013**

17. What are enzymes or biocatalysts? Give examples.

SHORT ANSWER Type I Questions

18. What are the essential and non-essential amino acids? Give one example of each type. **All India 2008 C; 2014 C; NCERT**

19. What are the common types of secondary structure of proteins? **NCERT**

20. Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form, is subjected to a physical change like change in temperature or a chemical change like, change in pH, denaturation of protein takes place. Explain the cause. **NCERT Exemplar**

Or

What is the effect of denaturation on the structure of proteins? **NCERT**

21. Activation energy for the acid catalysed hydrolysis of sucrose is 6.22 kJ mol^{-1} while the activation energy is only 2.15 kJ mol^{-1} when hydrolysis is catalysed by the enzyme sucrose. Explain. **NCERT Exemplar**

SHORT ANSWER Type II Questions

22. The melting points and solubility of amino acids in water are generally higher than that of the corresponding halo acids. Explain. **NCERT Intext**

23. Amino acids may be acidic, alkaline or neutral. How does this happen? What are essential and non-essential amino acids? Name one of each type. **All India 2010; Delhi 2010**

24. Define the following as related to proteins.
    (i) Peptide linkage
    (ii) Primary structure
    (iii) Denaturation **NCERT; All India 2015; Delhi 2014**

25. Write the function of the following enzymes.
    (i) Invertase
    (ii) Urease
    (iii) Maltase **NCERT Exemplar**

26. What are enzymes? Describe their functions. Name two diseases which are caused due to deficiency of enzymes. **All India 2016**

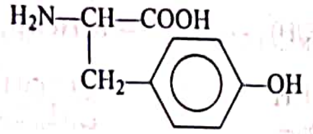
27. Define the following with an example of each **Delhi 2020, CBSE 2018**
    (a) Polysaccharides
    (b) Denatured protein
    (c) Essential amino acids

Or

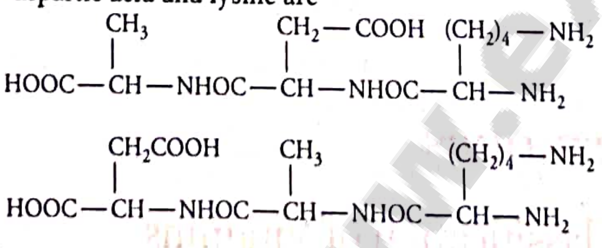
(a) Write the product when D-glucose reacts with conc. HNO_3.
(b) Amino acids show amphoteric behaviour. Why?
(c) Write one difference between α-helix and β-pleated structures of proteins.

HINTS AND EXPLANATIONS

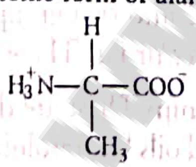
1. (*b*) Refer to page 418 (α-helix structure).
2. (*d*) Tyrosine has phenyl —OH group



3. (*b*) Except glycine (Gly), all the other naturally occurring α-amino acids are optically active.
4. (*c*) The functional unit that is repeated in a protein molecule is a peptide linkage.
5. (*d*) pH does not affect the primary structure of protein.
6. (*d*) Tertiary structure of protein are mainly stabilised by hydrogen bonds, disulphide bonds, van der Waals' forces and electrostatic forces of attraction.
7. (*d*) Coagulation of egg white, caused by heating and curdling of milk, caused by the acidity (of lactic acid) are examples of denaturation of protein. Clotting of blood is not an example of denaturation of protein.
8. (*c*) Enzymes are nitrogen containing high molecular weight organic compounds. Actually these are proteins.
9. α-amino acids forms polypeptide chain in proteins.
10. Amino acids contain both amino ($—NH_2$) and carboxyl (—COOH) groups, thus they react with both acids and bases. Hence, amino acids are amphoteric in nature.
11. Peptide linkage.
12. (i) The two tripeptides using amino acids alanine, aspartic acid and lysine are



(ii) The Zwitter ionic form of alanine is



13. Fibrous proteins have thread or fibre like structures whereas globular proteins have spherical shape.
14. **Fibrous protein** Keratin and myosin

    Globular protein Insulin and albumin
15. In α-helix, a polypeptide chain forms all possible hydrogen bonds by twisting into a right handed helix. On the other hand in β-pleated sheets, peptide chains are stretched out to nearly maximum extension and laid side by side by intermolecular hydrogen bonds.
16. Hydrogen bonding.
17. Enzyme or biocatalysts catalyse the biochemical reactions.
18. Refer to text on page 416.
19. The conformation which the polypeptide chain assume due to hydrogen bonding between $—\overset{\overset{\displaystyle O}{\|}}{C}—$ and NH group of the peptide bond is called **secondary structure of proteins.**

    These exist in two types of different structures:

    (i) **α-helix** Refer to text on pages 417-418.

    (ii) **β-pleated structure** Refer to text on page 418.
20. Refer to text on page 418.
21. Enzymes are the essential biological catalysts which are needed to catalyse biochemical reactions. Enzymes are needed only in small quantities for the progress of a reaction. Like chemical catalysts, enzymes reduces the magnitude of activation energy by providing alternative pathway, e.g. hydrolysis of sucrose, the enzyme sucrase reduces the activation energy from 6.22 kJ mol^{-1} to 2.15 kJ mol^{-1}. Thus, enzyme catalysed reactions occur at a much faster rate.
22. The amino acids exist as Zwitter ions ($H_3\overset{+}{N}—CHR—COO^-$) in aqueous solution. Due to this, dipolar salt like structure amino acids have strong dipole-dipole attractions.

    Thus, their melting points are higher than corresponding halo acids which do not have salt like character. Secondly, they interact strongly with H_2O due to their salt like character. As a result, polar amino acids dissolve in polar solvents like H_2O. Hence, the solubility of amino acids in water is higher than that of corresponding halo acids, which do not have any salt like character.
23. Amino acids may be acidic, basic or neutral depending upon the relative number of amino and carboxyl groups present in the molecule.

    Equal number of amino and carboxyl groups makes it neutral, more number of amino than carboxyl groups makes it basic and more carboxylic groups as compared to amino groups makes it acidic. Refer to text on page 576 for essential and non-essential amino acids.
24. (i) Refer to text on page 417.

    (ii) Refer to text on page 417.

    (iii) Refer to text on page 418.
25. (i) **Invertase** Hydrolysis of cane sugar.

    (ii) **Urease** Decomposition of urea into NH_3 and CO_2.

    (iii) **Maltase** Hydrolysis of maltose into glucose.

26. Enzymes are biological catalyst, they are composed of proteins. Enzymes are highly specific in nature. The two main functions are as follows :

(i) They lower the requirement of activation energy.

(ii) They speed up the rate of reaction.

e.g. Enzyme maltase catalyses maltose to glucose :

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} 2C_6H_{12}O_6.$$

(iii) Two diseases which are caused due to deficiency of enzymes are

(a) Phenyl ketone urea (PKU) (b) Albinism

27. (a) Carbohydrates which give a large number of monosaccharide units on hydrolysis are called polysaccharides, e.g. starch, cellulose, glycogen, etc. These are not sweet in taste, therefore they are also called **non-sugars**.

(b) Protein found in a biological system with a unique three-dimensional structure and biological activity, as native proteins. When a native protein is subjected to a physical change (like change in temperature) or a chemical change (like change in pH), its hydrogen bonds are disturbed. As the result, globules unfold and helix get uncoiled and protein loses its biological activity.

This is known as denaturation of protein. During denaturation, 2° and 3° structures are destroyed but 1° structure remains intact, e.g. coagulation of an egg white on boiling and curdling of milk caused due to the formation of lactic acid by the bacteria present in milk.

(c) Those amino acids which cannot be synthesised in the human body and are supplied through our diet (because they are required for proper health and growth) are called essential amino acids. e.g. Arginine lysine, etc.

Or (a) It is saccharic acid which is formed as per the reaction given below:

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \\ \text{D-Glucose} \end{array} \xrightarrow[\text{HNO}_3]{\text{Oxidation}} \begin{array}{c} COOH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \\ \text{Saccharic acid} \end{array}$$

(b) Amino acids may be acidic, basic or neutral depending upon the relative number of active amino and carboxyl group present in their molecule.

Equal number of amino and carboxyl groups makes it neutral, more amino group means basic and more carboxylic group means acidic amino acid.

Hence, amino acids show amphoteric behaviour.

(c) Difference between α-helix and β-pleated structures

α-helix Structure	β-pleated Structure
If the size of *R*-group is large, intramolecular H-bonds are formed between C=O of molecule and NH of amino acid in polypeptide chain that gives right handed α-helix structure, i.e. it is formed by the folding of a single polypeptide chain due to hydrogen bonding.	If size of *R*-group is small intermolecular H-bonds forms between C=O of polypeptide chain with N—H of other giving β-pleated sheet structure, i.e. it is formed by the folding in more than one polypeptide chain due to hydrogen bonding.

|TOPIC 3|
Vitamins, Nucleic Acids and Hormones

VITAMINS

These are the organic compounds required in small amounts in our diet but their deficiency causes specific diseases. Most of the vitamins cannot be synthesised in our body but plants can synthesise almost all of them. Hence, vitamins are considered as essential food factors. All the vitamins are generally available in our diet. They are generally regarded as organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism.

Vitamins are designated by alphabets A, B, C, D, etc. Some of them are further named as subgroups.

e.g. B_1, B_2, B_6, B_{12}, etc.

Classification of Vitamins

Vitamins are classified into two groups depending upon their solubility in water or fat. These are as follows :

(i) **Fat soluble vitamins** These are the vitamins which are soluble in fat and oils but insoluble in water. These are vitamins A, D, E and K. These are stored in liver and adipose (fat storing) tissues.

(ii) **Water soluble vitamins** These are the vitamins which are soluble in water. B groups vitamins and vitamin C are soluble in water, so they are grouped together.

Water soluble vitamins must be supplied regularly in diet, because they are readily excreted in urine and cannot be stored (except vitamin B_{12}) in our body.

Some important vitamins, their sources and deficiency diseases

Name of vitamins	Sources	Deficiency diseases
Vitamin A (Retinol)	Fish liver oil, carrots, butter and milk	Xerophthalmia (hardening of cornea of eye) and night blindness.
Vitamin B_1 (Thiamine)	Yeast, milk, green vegetables and cereals	Beri-beri (paralysis of legs, loss of appetite and retarded growth)
Vitamin B_2 (Riboflavin)	Milk, egg white, liver, kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin.
Vitamin B_6 (Pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
Vitamin B_{12} (Cyanocobalamin)	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin).
Vitamin C (Ascorbic acid)	Citrus fruits, amla and green leafy vegetables	Scurvy (bleeding of gums).
Vitamin D (Egrocalciferol)	Exposure to sunlight, fish and egg yolk.	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults).
Vitamin E (α- tocopherol)	Vegetable oils like wheat gram oil, sunflower oil, etc.	Increased fragility of RBCs and muscular weakness.
Vitamin H (Biotin)	Yeast, liver, kidney and milk.	Dermatitis, skin disease, loss of hair and paralysis.
Vitamin K (Phylloquinone)	Green leafy vegetables.	Increased blood clotting time.

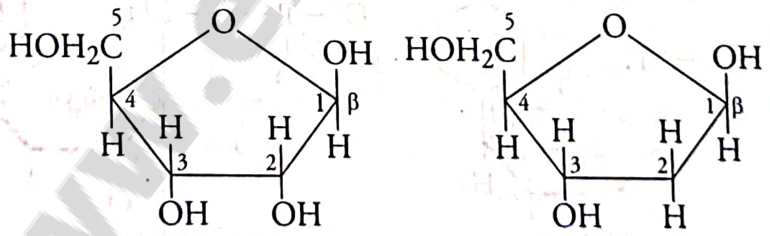
NUCLEIC ACIDS

Every generation of each and every species resembles its ancestors in many ways. Actually, the nucleus of a living cell is responsible for the transmission of inherent characters, also called **heredity.** The particles in the nucleus of the cell, responsible for heredity are called **chromosomes.** These are made up of proteins and another type of biomolecules called nucleic acids. Nucleic acids are of two types **deoxyribonucleic acid** (DNA) and **ribonucleic acid** (RNA). They are also called polynucleotides as they are made up of long chain polymers of **nucleotides.**

Chemical Composition of Nucleic Acids

On complete hydrolysis of DNA (or RNA), nucleic acid gives three different compounds:

(i) **Pentose sugar** DNA molecules contain, β-D-2-deoxyribose, a sugar moiety, whereas RNA contains, β-D-ribose.



β-D-ribose β-D-2-deoxyribose

(ii) **Phosphoric acid** It is the common product for both DNA and RNA hydrolysis

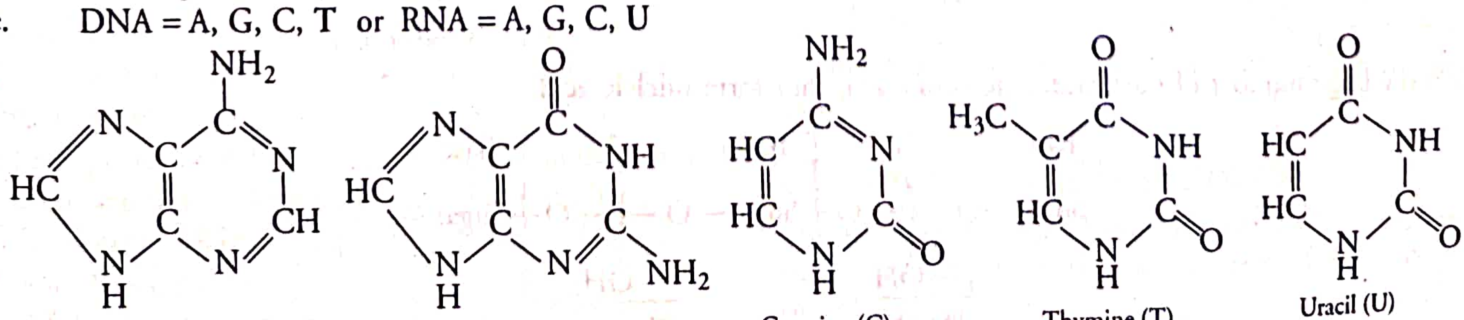
(iii) **Nitrogen base** Nitrogen containing heterocyclic compounds called nitrogenous base. Nitrogenous bases are of two types:

(a) **Purines** *Adenine (A) and Guanine (G)*

(b) Pyrimidines Uracil (U), Thymine (T) and Cytosine (C)

DNA and RNA both contain three common bases; adenine (A), guanine (G) and cytosine (C). Thymine (T) is present in DNA but in place of thymine, RNA contains uracil (U). So, there are four bases in each DNA and RNA.

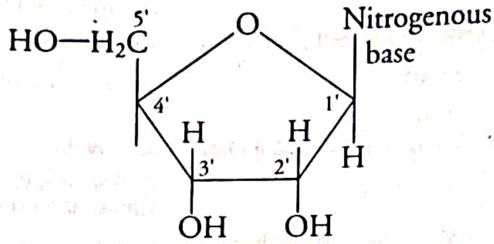
i.e. DNA = A, G, C, T or RNA = A, G, C, U



Adenine (A) Guanine (G) Cytosine (C) Thymine (T) Uracil (U)

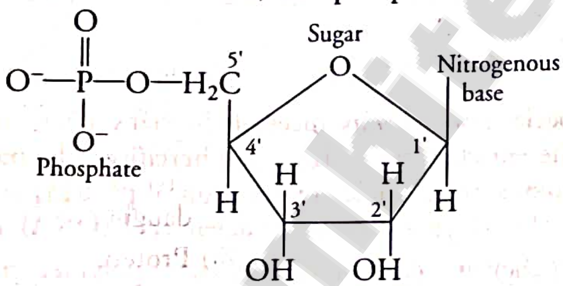
Structure of Nucleic Acids

Nucleoside A nucleoside consists of two basic components of nucleic acids; i.e. a pentose sugar and nitrogenous base. Actually, it is the unit in which base is attached to 1′ position of sugar. In nucleosides, the sugar carbons are numbered as 1′, 2′, 3′, etc., in order to distinguish these from the bases.



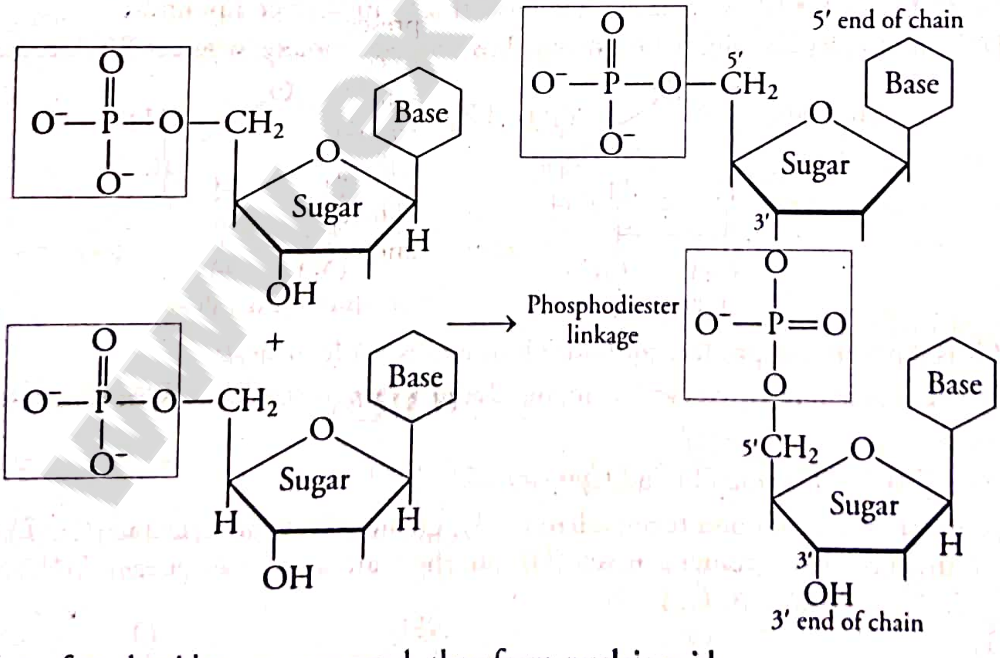
Structure of nucleoside

Nucleotide When nucleoside is linked to phosphoric acid at 5′ position of sugar moiety, a nucleotide is formed. Thus, a nucleotide contains three basic components of nucleic acids, i.e. a phosphoric acid, a nitrogenous base and a pentose sugar.

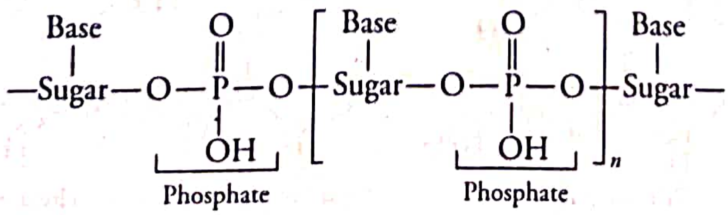


Structure of nucleotide

Nucleotides are joined together by phosphodiester linkage between 5′ and 3′ carbon atoms of the pentose sugar.



When the large number of nucleotides are connected, they form nucleic acid.



Nucleic acid or polynucleotide

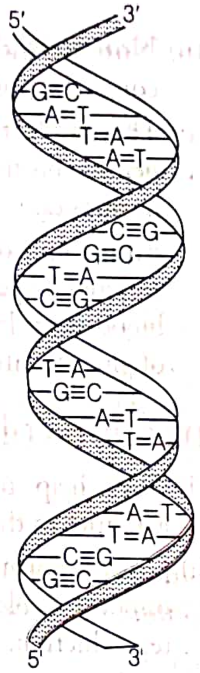
Structure of nucleic acid can be studied at two levels, i.e. primary and secondary:

Primary Structure

The information regarding the sequence of nucleotides in the chain of nucleic acid is called its primary structure.

Secondary Structure

James Watson and **Francis Crick** proposed a double stranded helical structure for DNA. According to this model, DNA consists of two separate polynucleotide strands leading in opposite directions (3′ or 5′). The polynucleotide chains of the double helix are held together by hydrogen bonds between pairs of bases.



Double strand helix structure for DNA

The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases.

Adenine of one strand is hydrogen bonded to thymine of the other through two hydrogen bonds whereas cytosine of one strand is hydrogen bonded with guanine of the other through three hydrogen bonds, i.e.

$$\underset{\text{2 hydrogen bonds}}{\underset{\uparrow}{A = T}} \quad \text{and} \quad \underset{\text{3 hydrogen bonds}}{\underset{\uparrow}{C \equiv G}}$$

In secondary structure of RNA, helices are present which are single-stranded but sometimes they fold back on themselves to form a double helix structure.

RNA molecules are of three types, i.e. **messenger RNA** (*m*RNA), **ribosomal RNA** (*r*RNA) and **transfer RNA** (*t*RNA). They all perform different functions.

DNA Fingerprinting

Each and every individual has unique fingerprints which are present on the tips of the fingers and have been used for the identification purposes.

A sequence of bases on DNA is also unique for a person and information regarding this, is called DNA fingerprinting.

The sequence on DNA is same for each and every cell of a body and hence, these sequence cannot be altered. Technique of DNA fingerprinting is used in the following ways:

(i) To determine the paternity of an individual.

(ii) To identify the racial groups to understand biological evolution better.

(iii) In forensic laboratories, for the identification of criminals.

(iv) To identify dead bodies in case of an accident by comparing the DNAs of parents and children.

Note Dr. Har Gobind Khurana shared the Nobel prize for medicine and physiology in 1968 with Marshall Nirenberg and Robert Holley for cracking the genetic code.

Biological Functions of Nucleic Acids

The important biological functions of nucleic acids are given below :

(i) **Heredity** DNA serves as the chemical basis of heredity and may be considered as reserve of genetic information.

DNA is mainly responsible for maintaining the identity of different species over millions of years.

(ii) **Replication** A DNA molecule is capable of self duplication (generally called replication) during cell division and identical DNA strands are transferred to daughter cells.

(iii) **Protein synthesis** It is an important function of nucleic acids in the cell. Actually, the proteins are synthesised by various RNA molecules in the cell but the message for the synthesis of a particular protein is present in DNA. The synthesis of RNA by the DNA to conduct the message is called **transcription**, and synthesis of protein by these RNA is called **translation**.

The biological functions of nucleic acids can be concluded as **central dogma of the molecular biology** and can be represented as below.

$$\text{Replication} \circlearrowright \text{DNA} \xrightarrow{\text{Transcription}} \text{RNA} \xrightarrow{\text{Translation}} \text{Protein}$$

HORMONES

These are the chemical substances, produced by endocrine glands in the body and are released directly in blood stream. From here, these are transported to the site of their action. These act as intercellular messengers and control various ody functions. Different endocrine glands which produce hormones are thyroid, pituitary, pancreas, testes and ovaries.

Classification of Hormones

On the basis of chemical constitution, the hormones are mainly divided into two classes, i.e. steroid and non-steroid hormones.

(i) **Steroid hormones** The compounds which are the derivatives of four ring systems and consisting of three cyclopentane rings are called **steroids**. Sex hormones, bile acids, etc., are steroid hormones.

- Steroid hormones can be further classified as sex hormones and adrenocortical hormones.

  (a) **Sex hormones** Sex hormones are mainly of three types, i.e. male sex hormone or androgen, female sex hormone or estrogen and pregnancy hormone or progesterone. Female sex hormone is responsible for the development of secondary female characteristics and participates in the control of menstrual cycle. Progesterone is responsible for preparing the uterus for the implantation of fertilized egg.

  (b) **Adrenocortical hormones or corticosteroids** These hormones are involved in the regulation of large number of biological activities such as carbohydrates, proteins and lipid metabolism, etc.

(ii) **Non-steroid hormones** These hormones do not contain steroid ring.

They are further classified as protein or peptide hormone, amino acid derivative or amine hormones.

An example of this type of hormone is insulin, secreted by pancreas, its function is to lower the blood sugar level by increasing the rate of conversion of glucose into glycogen.

Functions of Hormones

(i) They help to maintain the balance of biological activities in the body.

(ii) Growth hormone and sex hormone play an important role in growth, development and reproduction.

(iii) Sex hormones are also responsible for the development of secondary sexual characters.

TOPIC PRACTICE 3

OBJECTIVE Type Questions

1. Which of the following is a fat soluble vitamin?
(a) Vitamin A (b) Vitamin B_6
(c) Vitamin C (d) Vitamin B_2

2. Ascorbic acid is
(a) protein (b) enzyme
(c) hormone (d) vitamin C

3. Which of the following disease is caused by the deficiency of vitamin E?
(a) Beri-beri (b) Rickets
(c) Scurvy (d) Muscular weakness

4. Disease caused due to deficiency of vitamin C is
(a) beri-beri
(b) night blindness
(c) T.B.
(d) scurvy

5. Which of the following acids is a vitamin? **NCERT Exemplar**
(a) Aspartic and (b) Ascorbic acid
(c) Adipic acid (d) Saccharic acid

6. Nucleotides are composed of a **CBSE 2021 (Term I)**
(a) pentose sugar and phosphoric acid
(b) nitrogenous base and phosphoric acid
(c) nitrogenous base and a pentose sugar
(d) nitrogenous base, a pentose sugar and phosphoric acid

7. Select the base which is not common between DNA and RNA.
(a) Adenine (A) (b) Guanine (G)
(c) Cytosine (C) (d) Thymine (T)

8. Nucleic acids are the polymers of **NCERT Exemplar**
(a) nucleosides (b) nucleotides
(c) bases (d) sugars

VERY SHORT ANSWER Type Questions

9. Why cannot vitamin C be stored in our body? **NCERT Intext**

Or Why must vitamin C be supplied regularly in the diet? **NCERT Exemplar**

10. Name the deficiency diseases resulting from lack of vitamins A and E in the diet. **Delhi 2013**

11. Write the name of disease caused by the deficiency of vitamin B_{12}. **All India 2015**

12. Deficiency of which vitamin causes scurvy? **All India 2014**

13. Deficiency of which vitamin causes rickets? **Delhi 2014**

Or Write the name of vitamin whose deficiency causes bone deformities in children. **Delhi 2015**

14. A vitamin is soluble in water and its deficiency in the body causes beri-beri. Identify the vitamin.

15. Name the base that is present in RNA and not in DNA?

16. Define nucleotides.

Delhi 2014

17. Name two fat soluble vitamins, their sources and the diseases caused due to their deficiency in diet.

18. Deficiency of which vitamin causes xerophthalmia and cheiolosis? Give its sources also.

19. Why does vitamin B must be supplied regularly in diet?

20. Why does nucleic acids are called polynucleotides?

21. A man is suffering from muscular weakness and fragility of RBCs. Which kind of food intake should he increase?

22. Name the base that is found in the nucleotide of RNA only. **All India 2014**

SHORT ANSWER Type I Questions

23. In nucleoside, a base is attached at 1′ position of sugar moiety. Nucleotide is formed by linking of phosphoric acid unit to the sugar unit of nucleoside. At which position of sugar unit is the phosphoric acid linked in a nucleoside to give a nucleotide? **NCERT Exemplar**

24. Name all the bases present in RNA and DNA?

25. What products would be formed when a nucleotide from DNA containing thymine is hydrolysed? **NCERT Intext**

26. What are the different types of RNA molecules which perform different functions? **Delhi 2013**

Or What are the different types of RNA found in the cell? **NCERT**

27. Mention the biological importance of insulin.

28. Why are vitamins A and C essential to us? Give their important sources. **NCERT**

29. The two strands of DNA are not identical but are complementary. Explain. **NCERT**

30. Write the important structural and functional differences between DNA and RNA. **NCERT; Delhi 2013**

31. What is the difference between hormones and vitamins?

SHORT ANSWER Type II Questions

32. (i) Write the structural difference between starch and cellulose.
(ii) What type of linkage is present in nucleic acid?
(iii) Give one example each for fibrous protein and Globular protein. **All India 2016**

33. How are vitamins classified? Name the vitamin responsible for the coagulation of blood. **NCERT**

34. What are nucleic acids? Mention their two important functions. **NCERT**

35. What is the difference between a nucleoside and a nucleotide? **NCERT**

36. (i) Write the name of two monosaccharides obtained on hydrolysis of lactose sugar.
(ii) Why vitamin C can not be stored in our body?
(iii) What is the difference between a nucleoside and nucleotide? **Delhi 2020, 2016**

37. (i) What type of linkage is present in disaccharides?
(ii) Write one source and deficiency disease of vitamin B_{12}.
(iii) Write the difference between DNA and RNA. **Delhi 2017 C**

HINTS AND EXPLANATIONS

1. *(a)* Vitamin A is a fat soluble vitamin. It is insoluble in water. Fat soluble vitamins are A, D, E and K.

2. *(d)* Vitamin C is called ascorbic acid.

3. *(d)* Muscular weakness is caused by the deficiency of vitamin E.

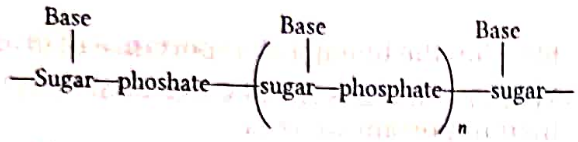
4. *(d)* Due to deficiency of vitamin C, gums start bleeding, this is scurvy disease.

5. *(b)* Ascorbic acid is the chemical name of vitamin C. While others are not vitamins. Aspartic acid is an amino acid. Adipic acid is a dicarboxylic acid having 8 carbon chain. Saccharic acid is a dicarboxylic acid obtained by oxidation of glucose using HNO_3.

6. *(d)* Nucleotides are composed of a nitrogenous base, a pentose sugar and phosphoric acid.

7. (d) DNA contains four bases, i.e. Adenine (A), Guanine (G) Cytosine (C) and Thymine (T). RNA also contains four bases, the first three bases are same as in DNA, but the fourth one is uracil (U).

8. *(b)* Nucleic acids are polymer of nucleotides in which nucleic acids are linked together by phosphodiester linkage.



e.g. DNA, RNA etc.

9. Vitamin C cannot be stored in our body because vitamin C is soluble in water, it excreted readily in urine and hence, cannot be stored in the body. Thus, vitamin C must be supplied regularly through diet.

10. Deficiency disease due to vitamin A-Night blindness.
Deficiency disease due to vitamin E-absorption of dietary fat.

11. Pernicious anaemia

12. Deficiency of vitamin C causes scurvy.

13. Vitamin D **14.** Vitamin B_1 (Thiamine) **15.** Uracil.

16. When nucleoside is linked to phosphoric acid as 5′ position of sugar moiety, a nucleotide is formed.

17. Vitamin A and D are fat soluble vitamins.
Source of Vitamin-A = Carrots, milk;
Deficiency disease: Night blindness
Source of Vitamin-D = Fish, egg yolk ;
Deficiency disease: Rickets

18. Xerophthalmia is caused by vitamin-A while cheiolosis is caused by vitamin D.

19. Because it is a water soluble vitamin.

20. They are made up of long chain polymers of nucleotides.

21. He should increase in take of vegetable oils.

22. Uracil base is found in the nucleotide of RNA only.

23. Phosphoric acid unit is linked at 5′ position of sugar moiety of a nucleoside to form nucleotide.

24. Refer to text on page 423.

25. Complete hydrolysis of DNA containing thymine yields a pentose sugar (β-D-2-deoxyribose), phosphoric acid and nitrogeneous base thymine.

26. Three different types of RNA molecules are as follows:
(i) Messenger RNA (*m*RNA) (ii) Transfer RNA (*t*RNA)
(iii) Ribosomal RNA (*r* RNA)

27. Controls the metabolism of glucose in the body and maintains glucose level in the blood.

28. Refer to text on page 422.

29. Refer to text on page 425.

30. **Structural differences** The main structural differences between DNA and RNA are as follows
(i) The sugar moiety present in DNA is β-D-2-deoxyribose, whereas in RNA molecule, it is β-D-ribose.
(ii) DNA has a double stranded helical structure, while RNA has a single stranded helical structure.
(iii) DNA contains cytosine and thymine as pyrimidine bases, whereas RNA has cytosine and uracil as pyrimidine bases.

Functional difference DNA controls the transmission of hereditary effects while RNA controls the synthesis of proteins.

31. The main points of differences are listed below :

	Hormones	Vitamins
(i)	They are produced in the ductless (endocrine) glands, e.g. testes of males and ovaries of females.	They are not produced in the body, have to be supplied in food (except vitamin D which may be supplied in the food or produced in skin by irradiation, of sterols present in oils and fats, with UV light).
(ii)	They are not stored in the body but are continuously produced.	They may remain stored (except vitamin C and some vitamins of group B) to fight against the diseases.

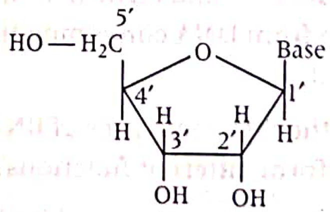
32. (i) Starch is a disaccharide of two components amylose and amylopectin, both are made of D-glucose units linked through α-glycosidic units. Amylose is water soluble while amylopectin is not.
Cellulose on the other hand is a polymer of straight chain β-D-glucose which consist about 300-3000 units of glucose.
(ii) Phosphodiester-linkage.
(iii) Fibrous protein ⟶ Keratin
Globular protein ⟶ Insulin.

33. **Classification of vitamins** Refer to text on page 422.
Vitamin K is responsible for coagulation of blood.

34. Refer to text on pages 423 and 425.

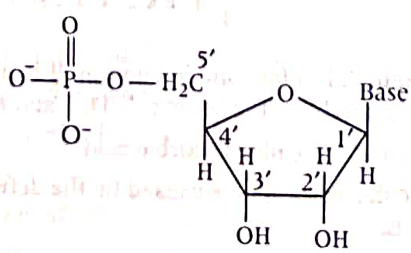
35. Refer to text on page 424.

36. (i) D-glucose and D-galactose.
(ii) Since, vitamin-C is a water soluble vitamin, it is excreted out through urine, hence cannot be stored.
(iii) **Nucleoside** A unit formed by the attachment of a base to 1' position of sugar known as nucleoside.



(Nucleoside)

Nucleotide When nucleoside is linked to phosphoric acid at 5′ position of sugar moiety, a nucleotide is obtained. They are joined together by phosphodiester linkage between 5′ and 3′ carbon atoms of the pentose sugar.



(Nucleotide)

37. (i) Glycosidic linkages.
(ii) Refer to text on page 423.
(iii) Refer to text on pages 423.

SUMMARY

- Carbohydrates are the polyhydroxy aldehyde or ketones. They are called hydrates of carbon and have general formula of $C_x(H_2O)_y$.
- **Monosaccharides** are the simplest carbohydrates, e.g. glucose, fructose etc.
- **Oligosaccharides** are made up of 2-10 monomer monosaccharide units, e.g. sucrose, lactose etc.
- **Polysaccharides** are made up of more than 10 monomer units, e.g. glycogen, starch, cellulose etc.
- Carbohydrates having free functional group aldehyde or ketone reduce Fehling's solution and Tollen's reagent and thus are called reducing sugars.
- Glucose ($C_6H_{12}O_6$) is an aldohexose, as it has aldehydic group and six C-atoms, dextrorotatory in nature and is also called dextrose.
- It can be prepared by hydrolysis of cane sugar (sucrose) and starch.
- Cyclic structure of glucose resembles to pyran and hence it is also called glucopyranose.
- Glucose oxidises with Br_2 water to give gluconic acid and with HNO_3 to give glucaric acid.
- It reduces both Fehling's solution and Tollen's reagent also forms osazone upon reaction with phenyl hydrazine.
- Fructose ($C_6H_{12}O_6$) is a ketohexose and differs from glucose by having keto group instead of aldehyde group (as in glucose).
- Natural fructose (laevulose) is laevorotatory and can be prepared by hydrolysis of inulin or sucrose. Its cyclic structure resembles with furan, hence also called **fructofuranose**.
- Sucrose is disaccharide of glucose and fructose monomer.
- The two monomer units in a disaccharide (or in any polysaccharide) is joined by a linkage called **glycosidic linkage**.
- Solution of sucrose is dextrorotatory but that of its hydrolysed product (glucose + fructose) is laevorotatory. This observation is called **inversion of cane sugar**.
- **Proteins** are the polymers of α-amino acids.
- Amino acids are essentialy formed of two functional groups called amino (—NH_2) group and carboxyl (—COOH) group.
- Amino acid forms Zwitter ion, in which both positive and negative charges are present but molecules acts as a neutral one.
- Amino acid that cannot be synthesised body and is required to be taken in our diet is called essential amino acid, e.g. val, leu, lys etc.
- The linkage that connects two amino acids is called peptide (or amide) bond.
- Amino acid through peptide linkage form polypeptide (upto 100 amino acids) which further link to form protein.
- **Primary structure** of protein is simply the formation of peptide bond between amino acids to form peptide.
- **Secondary** structure form three dimensional configuration of peptide chains involving H— bonds.
- **Tertiary structure** defines overall shape of a protein molecules. It involves H-bond, ionic bond, disulphide bond and hydrophobic bond.
- **Quaternary structure** involve assembling of two of more polypeptide chains. It involves H-bond, ionic bond and hydrophobic bond.
- **Fibrous proteins** are elongated and insoluble in water, e.g. keratin, collagen etc.
- **Globular proteins** are spherical and soluble in water, e.g. myoglobin, albumin etc.
- **Enzymes** are made up of proteins and act as a biocatalysts.
- The optimum temperature for working of enzymes is 37°(310 K) and optimum pH is 7.4.
- Vitamins are small organic molecules that are required for the proper functioning of the cell.
- Water soluble vitamins include vitamin B and vitamin C, vitamin A, D, E and K are fat soluble.
- **Nucleic acids** include DNA (deoxyribonucleic acid) and RNA (ribonucleic acid). These are composed of nitrogeneous base, sugar and phosphate group.
- Sugar and nitrogeneous base are combinely called **nucleoside**, where nucleoside and phosphate group is combinely called **nucleotide**. Therefore, nucleic acids are also called polynucleotides.
- Nitrogeneous bases are of two types : **Purine** – adenine (A) and guanine (G) **Pyrimidine**-cytosine (C), thymine (T) and uracil (U)
- The primary structure of nucleic acids is formed by nucleotides joined by the phosphodiester linkage.
- The secondary structure of nucleic acid is the coiled configuration of polynucleotidic chain, with the help of H-bonds.
- The two strands of DNA are complementary where adenine of one strand is connected to thymine (T) of the other one. While cytosine (C) of one strand is connected to guanine (G) of the other one.
- DNA and RNA replicate themselves to carry genetic information to next generation. DNA and RNA are also involved in protein synthesis.
- **Hormones** are the chemical substance secreted by ductless glands. These participate in biochemical reactions and control physiological process.
- Steriodal hormones include sex hormones and corticoids while non-steroid hormones include peptide hormone (insulin glucogen, oxytocin etc.) and amino acid derivatives (thyroxine, adrenaline etc).

CHAPTER PRACTICE

OBJECTIVE Type Questions

1 Name the reagent and condition required for carrying out of the following reaction.

$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \longrightarrow \underset{n\text{-hexane}}{CH_3-(CH_2)_4-CH_3}$$

(a) HF (b) HCl (c) HBr (d) HI

2 What happens to the glucose on heating with Fehling's solution?

(a) Oxidation (b) Reduction
(c) Decomposition (d) Condensation

3 Pyridoxin is also known as

(a) vitamin B_2 (b) vitamin B_6
(c) vitamin B_{12} (d) vitamin B_1

4 Which of the following vitamin is responsible for beri-beri disease?

(a) A (b) B_1 (c) K (d) D

5 Match the following columns.

	Column I		Column II
A.	Amino acids	1.	Protein
B.	Thymine	2.	Nucleic acid
C.	Insulin	3.	DNA
D.	Phosphodiester linkage	4.	Zwitter ion
E.	Uracil		

Which of the following is the best matched options? **CBSE SQP (Term I)**

Codes

	A	B	C	D
(a)	1	4	3	2
(b)	4	3	1	2
(c)	4	4	1	2
(d)	1	3	4	2

6 The bases that are common in both DNA and RNA are **CBSE 2021 (Term I)**

(a) adenine, guanine and cytosine
(b) adenine, guanine and thymine
(c) adenine, uracil and cytosine
(d) guanine, uracil and thymine

CASE BASED Questions

Case I

Adenosine triphosphate (ATP) is the energy-carrying molecule found in the cells of all living things. ATP captures chemical energy obtained from the breakdown of food molecules and releases it to fuel other cellular processes. ATP is a nucleotide that consists of three main structures: the nitrogenous base, adenine; the sugar, ribose; and a chain of three phosphate groups bound to ribose.

The phosphate tail of ATP is the actual power source which the cell taps. Available energy is contained in the bonds between the phosphates and is released when they are broken, which occurs through the addition of a water molecule (a process called hydrolysis). Usually only the outer phosphate is removed from ATP to yield energy; when this occurs ATP is converted to adenosine diphosphate (ADP), the form of the nucleotide having only two phosphates.

The importance of ATP (adenosine triphosphate) as the main source of chemical energy in living matter and its involvement in cellular processes has long been recognized. The primary mechanism whereby higher organisms, including humans, generate ATP is through mitochondrial oxidative phosphorylation. For the majority of organs, the main metabolic fuel is glucose, which in the presence of oxygen undergoes complete combustion to SO_2 and H_2O :

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6O_2 + 6H_2O + \text{Energy}$$

The free energy (ΔG) liberated in this exergonic (ΔG is negative) reaction is partially trapped as ATP in two consecutive processes: glycolysis (cytosol) and oxidative phosphorylation (mitochondria). The first produces 2 moles of ATP per mole of glucose, and the second 36 moles of ATP per mol of glucose. Thus, oxidative phosphorylation yields 17-18 times as much useful energy in the form of ATP as can be obtained from the same amount of glucose by glycolysis alone.

The efficiency of glucose metabolism is the ratio of amount of energy produced when 1 mols of glucose oxidised in cell to the enthalpy of combustion of glucose. The energy lost in the process is in the form of heat. This heat is responsible for keeping us warm.

The following questions are multiple choice questions. Choose the most appropriate answer :

7. Cellular oxidation of glucose is a:
(a) spontaneous and endothermic process
(b) non-spontaneous and exothermic process
(c) non-spontaneous and endothermic process
(d) spontaneous and exothermic process

8. What is the efficiency of glucose metabolism if 1 mole of glucose gives 38 ATP energy?(Given: The enthalpy of combustion of glucose is 686 kcal,
1 ATP = 7.3 kcal)
(a) 100% (b) 38% (c) 62% (d) 80%

9. Which of the following statement is true?
(a) ATP is a nucleoside made up of nitrogenous base adenine and ribose sugar.
(b) ATP consists the nitrogenous base, adenine and the sugar, deoxyribose.
(c) ATP is a nucleotide which contains a chain of three phosphate groups bound to ribose sugar.
(d) The nitrogenous base of ATP is the actual power source.

10. Nearly 95% of the energy released during cellular respiration is due to
(a) glycolysis occurring in cytosol
(b) oxidative phosphorylation occurring in cytosol
(c) glycolysis in occurring mitochondria
(d) oxidative phosphorylation occurring in mitochondria

11. Which of the following statements is correct ?
(a) ATP is a nucleotide which has three phosphate groups while ADP is a nucleoside which three phosphate groups.
(b) ADP contains a nitrogenous bases adenine, ribose sugar and two phosphate groups bound to ribose.
(c) ADP is the main source of chemical energy in living matter.
(d) ATP and ADP are nucleosides which differ in number of phosphate groups.

Case II

EVIDENCE FOR THE FIBROUS NATURE OF DNA

The basic chemical formula of DNA is now well established. As shown in Figure 1 it consists of a very long chain, the backbone of which is made up of alternate sugar and phosphate groups, joined together in regular 3′ 5′ phosphate di-ester linkages.

To each sugar is attached a nitrogenous base, only four different kinds of which are commonly found in DNA. Two of these – adenine and guanine – are purines, and the other two – thymine and cytosine – are pyrimidines. A fifth base, 5-methyl cytosine, occurs in smaller amounts in certain organisms, and a sixth, 5-hydroxy-methyl-cytosine, is found instead of cytosine in the T even phages (Wyatt and Cohen, 1952).

It should be noted that the chain is unbranched, a consequence of the regular internucleotide linkage. On the other hand the sequence of the different nucleotides is, as far as can he ascertained, completely irregular. Thus, DNA has some features which are regular, and some which are irregular.

A similar conception of the DNA molecule as Aided by a Fellowship from the National Foundation for Infantile Paralysis.

Long thin fiber is obtained from physico-chemieal analysis involving sedimentation, diffusion, light scattering, and viscosity measurements. These techniques indicate that DNA is a very asymmetrical structure approximately 20 A wide and many thousands of angstroms long.

Estimates of its molecular weight currently center between 5×10^6 and 10^7 (approximately 3×10^4 nucleotides). Surprisingly each of these measurements tend to suggest that the DNA is relatively rigid, a puzzling finding in view of the large number of single bonds (5 per nucleotide) in the phosphate-sugar back-

D.N.A.

BASE—SUGER
>PHOSPHATE
BASE—SUGER
>PHOSPHATE
BASE—SUGER
>PHOSPHATE
BASE—SUGER
>PHOSPHATE
BASE—SUGER

Chemical formula (diagrammatic) of a single chain of deoxyribonucleic acid.

12. Purines present in DNA are
(a) adenine and thymine
(b) guanine and thymine
(c) cytosine and thymine
(d) adenine and guanine

13. DNA molecule has .... internucleotide linkage and .... sequence of the different nucleotides.
(a) regular , regular
(b) regular , irregular
(c) irregular , regular
(d) irregular , irregular

14. DNA has a .... backbone.
(a) phosphate -purine
(b) pyrimidines- sugar
(c) phosphate- sugar
(d) purine- pyrimidine

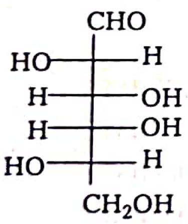
15. Out of the four different kinds of nitrogenous bases which are commonly found in DNA, ... has been replaced in some organisms.
(a) adenine
(b) guanine
(c) cytosine
(d) thymine

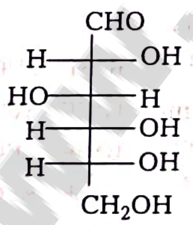
Case III

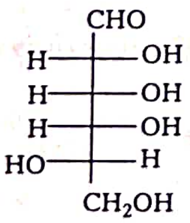
Carbohydrates are polyhydroxy aldehydes or ketones and are also called saccharides. Glucose is an example of monosaccharides. Glucose ($C_6H_{12}O_6$) is an aldohexose and its open chain structure was assigned on the basis of many reactions as evidences like presence of carbonyl group, presence of straight chain, presence of five —OH groups etc. Glucose is correctly named as D-(+)-glucose. Glucose is found to exist in two different crystalline forms which are named as α and β. Despite having the aldehyde group, glucose does not give 2, 4-DNP test. **CBSE 2021 (Term I)**

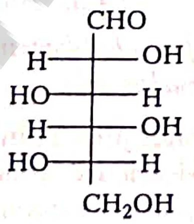
The following questions are multiple choice questions. Choose the most appropriate answer :

16 Which of the following represents D-(+)-glucose?

(a) 

(b) 

(c) 

(d) 

17 Glucose on oxidation with HNO_3 gives a dicarboxylic acid called saccharic acid. This result validates the fact that glucose possesses
(a) –CHO group
(b) –OH group
(c) a straight chain
(d) both — CHO and — CH_2OH groups at the terminals of the chain

18. The pentaacetate of glucose does not react with H_2N—OH indicating the absence of
(a) –OH group
(b) –CHO group
(c) –COOH group
(d) – CH_2OH group

Case IV

Glucose is an aldohexose. It can occur freely as well as in combined form in the nature. It is present in sweet fruits and honey. It is also present in quantities in ripe grapes. As glucose is an aldohexose, it consists of six C-atoms and an aldehyde group.

It is the most abundant organic compound on the earth and used as an immediate source of energy for all metabolic reactions in the animals.

It was found that glucose forms a six membered ring in which —OH at C-5 is involved in the ring formation. The cyclic six membered structure of glucose is known as pyranose structure. It is analogous to pyran which is a cyclic organic compound with one oxygen atom and five carbon atoms in the ring.

In the question that follow Assertion and Reason are given. Reason is purported to the explaination for Assertion. Study carefully and then mark your answers, according to the codes given below.

Marks your answer as :
(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

19 **Assertion** Glucose can be prepared from sucrose.
Reason $\underset{\text{Sucrose}}{C_{12}H_{12}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

20 **Assertion** The aldehyde group is absent in the pentacetate of D-glucose?
Reason It has ketone group.

Or **Assertion** When glucose is treated with HI from hexane.
Reason Due to presence of amine acids.

21 **Assertion** The saccharic acid formed when glucose undergoes oxidation.
Reason Due to presence of amino acids.

22 **Assertion** The glucose has structure of open-chain.
Reason —COOH at the end of chain.

ASSERTION and REASON

Directions (Q. Nos. 23-28) *In the following questions. an Assertion (A) is followed by a corresponding Reason (R) Use the following keys to choose the appropriate answer.*

(a) Both (A) and (R) are correct, (R) is the correct explanation of (A).
(b) Both (A) and (R) are correct, (R) is not the correct explanation of (A).
(c) (A) is correct; (R) is incorrect.
(d) (A) is incorrect; (R) is correct.

23 **Assertion** The two strands are complementary to each other. **CBSE SQP 2021**

Reason The hydrogen bonds are formed between specific pairs of bases.

24 **Assertion** (A) The coagulation of egg white occur on boiling.

Reason (R) Denaturation of protein is occur when its native form is subjected to physical change or chemical change.

25 **Assertion** (A) In the presence of enzyme, substrate molecule can be attacked by the reagent effectively.

Reason (R) Active sites of enzymes hold the substrate molecule in a suitable position.

26 **Assertion** (A) Vitamins A, D, E and K are stored in liver and adipose tissue.

Reason (R) Vitamins A, D, E and K are soluble in fats and oils.

27 **Assertion** (A) The two strands of DNA are complementary to each other.

Reason (R) Adenine forms hydrogen bonds with guanine and thymine forms hydrogen bonds with cytosine.

28 **Assertion** (A) When RNA is hydrolysed, there is no relationship among the quantities of different bases obtained.

Reason (R) RNA molecules are of three types and they perform different functions.

VERY SHORT ANSWER Type Questions

29 What is inversion of sugar?

30 Name two carbohydrates that are branched polymers of glucose.

31 In representation of D-(+)-glucose, what does 'D' represents?

32 How do amino acids form proteins?

33 Name the protein and its shape which is present in muscles.

34 What type of proteins acts as enzymes?

35 Which of the following biomolecule is soluble in water? collagen, myosin and albumin

36 What type of interactions stabilises β-pleated keratin structure?

37 What type of interactions stabilises the fibrous proteins?

38 Which enzyme converts glucose into ethyl alcohol?

39 Deficiency of which vitamin causes osteomalacia?

SHORT ANSWER Type I Questions

40 Name and define the linkage connecting monosaccharide units in a polysaccharide.

41 Amylopectin and glycogen both have branched structures. How do they differ from one another?

42 Why do proteins form an indispensable part of our food?

43 (i) Name an amino acid which is optically active.
(ii) Draw the Zwitter ion of an essential amino acid which contains phenyl ring.

44 Mention the type of linkages responsible for the formation of the following:
(i) Primary structure of proteins
(ii) α-helix formation
(iii) β-pleated sheet structure

45 Why does a native protein loses its biological activity on heating?

46 What role do enzymes have in the functioning of our bodies?

47 Name the chemical components which constitute nucleotides. Write any two functions of nucleotides in a cell.

SHORT ANSWER Type II Questions

48 (i) What is the biological effect of proteins on denaturation?
(ii) Amylase present in the saliva becomes inactive in the stomach. Give reason.

49 Write the four characteristic features of enzymes. Name a disease which is caused by the deficiency of a particular enzyme.

50 (i) Which vitamin is concerned with antisterility?
(ii) Write the chemical name of B_1 and name the disease caused by its deficiency.

51 (i) Explain the role of nucleic acids in replication.

(ii) Name the types of bases in nucleotides of RNA.

LONG ANSWER Type Questions

52 A compound A ($C_6H_{12}O_6$) is oxidised by bromine water into monobasic acid. It also reduces Tollen's reagent and reacts with HCN to give a compound B which on hydrolysis gives a compound C. On treating C with HI/red P, n-heptanoic acid is obtained. Compound A on treatment with excess phenyl hydrazine gave D-glucoszone. Name the compound A and draw its cyclic from.

ANSWERS

1 (*d*) **2** (*a*) **3** (b) **4** (b) **5** (b) **6** (d)

7 (*d*) Cellular oxidation of glucose is a catabolic pathway during which six carbon glucose molecule is split into two 3 carbon sugars which are then oxidised and rearranged by a stepwise metabolic process that produces two molecules of pyruvic acid. It is spontaneous and exothermic process.

8 (*b*) Energy of 1 ATP = 7.3 kcal

Energy of 38 ATP = 7.3 × 38 = 262 kcal

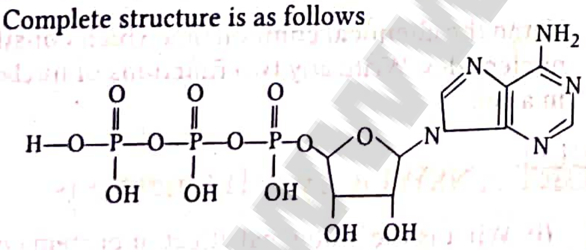
Energy of glucose = 686 kcal

Thus, the efficiency of glucose metabolism is

$$= \frac{262}{686} \times 100 = 38\%$$

9 (*c*) ATP is a nucleotide which contains a chain of three phosphate groups bound to ribose sugar.

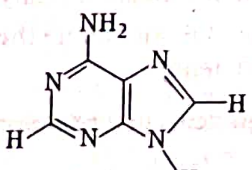
Complete structure is as follows



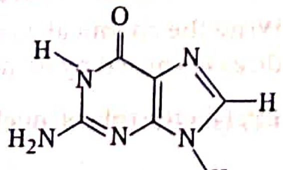
10 (*d*) Nearly 95% of the energy released during cellular respiration is due to mitochondrial oxidative phosphorylation.

11 (*b*) ADP contains a nitrogenous bases adenine, ribose sugar and two phosphate groups bound to ribose.

12 (*d*) Adenine and guanine are two purine base present in DNA. Structure as follows



Adenine



Guanine

13 (*b*) DNA molecule has regular internucleotide linkage and the sequence of different nulceotides as far as ascertained and completely irregular.

14 (*c*) Backbone of DNA is made up of alternate sugar and phosphate groups, joined together in regular 3'5' phosphate di-ester linkages.

15 (*c*) Cytosine has been replaced in some organisms, is commonly found in DNA. 5 methylcytosine and 5-hydroxymethylcytosine is found instead of cytosine in the T even phases.

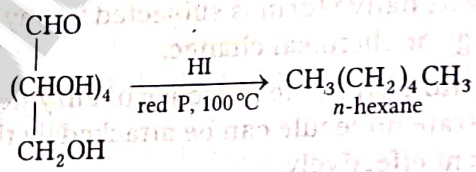
16 (*b*) **17** (*b*) **18** (*b*)

19 (*a*) Both (A) and (R) are true and (R) is correct explanation of (A).

20 (*c*) The pentacetate of glucose does not react with hydroxyl amine (NH_2OH) which shows that aldehyde (—CHO) group is not present in glucose pentacetate.

Only (A) is correct.

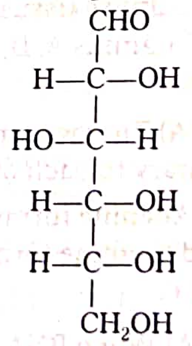
Or (*e*) *n*-hexane is formed.



Only (A) is correct.

21 (*c*) Only (A) is correct.

22 (*c*) Open chain strcuture of glucose is



Only (A) is correct.

23 (*a*) The two strands of DNA are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine of one strand is hydrogen bonded to thymine of the other through two hydrogen bonds whereas cytosine of one strand is hydrogen bonded with guanine of the other through 3 hydrogen bonds.

$A{=}T$ and $C{\equiv}G$

$A{=}T$ ↓ 2 hydrogen bonds; $C{\equiv}G$ ↓ 3 hydrogen bonds

Hence, both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

24 (*a*) When a protein in its native form is subjected to physical change like change in temperature or chemical

change like change in pH, the hydrogen bonds are disturbed.

Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein. The coagulation of egg white on boiling is the common example of denaturation. Thus, both (A) and (R) are correct explanation of (A).

25 (*a*) In the presence of an enzyme, substrate molecule can be attacked by the reagent effectively because active sites of enzymes hold the substrate molecule in a suitable position. Thus, both (A) and (R) are correct explanation of (A).

26 (*b*) Some vitamins are soluble in fat and oils but insoluble in water. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues. Hence, Both (A) and (R) are correct but (R) is not the correct explanation of (A).

27 (*c*) Two strands of DNA are complementary to each other because the hydrogen bonds are formed between specific pairs of bases.

Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine. Hence, (A) is correct but (R) is incorrect.

28 (*b*) When RNA is hydrolysed, there is no relationship among the quantities of four different bases obtained because in RNA, the bases don't occur in pairs as it is a single stranded strcuture. RNA molecules are of three types and they perform different functions. They are named as messenger RNA (*m*-RNA), ribosomal RNA (*r*-RNA) and transfer RNA (*t*-RNA). Thus, both A and R are correct but R is not the correct explanation of A.

29 Sucrose on hydrolysis give equimolar mixture of D-(+)-glucose and D-(−)-fructose known as invert sugar and the process is called as inversion of sugar.

30 Glycogen and amylopectin.

31 '*D*' represents the confinguration.

32 More than 100 amino acid residues are joined together by peptide linkage to form a linear chain polymer (protein).

33 Fibrous protein (myosin).

34 Globular proteins **35** Albumin

36 Intermolecular hydrogen bonding stabilises β-pleated keratin structure.

37 They are held together by hydrogen and disulphide bonds.

38 Zymase enzyme.

39 Deficiency of vitamin-D causes Osteomalacia.

40 Refer to text on page 411.

41 Glycogen consist of 10-15 glucose units while amylopectin consist of 20-25 glucose unit.

42 [**Hint** Providing strength to the cells and tissues.]

43 (i) Glycine (ii) Refer to text on page 417.

44 (i) Refer to text on page 417.
(ii) Refer to text on page 418.
(iii) Refer to text on page 418.

45 Refer to text on page 418.

46 **Hint** Aids indigestion and metabolism.

47 Refer to text on pages 424 and 425.

48 (i) Refer to text on page 418.
(ii) **Hint** Stomach has pH range 1-3

49 (i) Refer to text on page 418 and 419.
(ii) Disease phenyl ketone urea (PKU) by the deficiency of phenylalanine hydroxylose.

50 (i) Vitamin E (ii) Refer to text on page 422.

51 (i) Refer to text on pages 425.
(ii) Refer to text on page 424.

52 **Hint** cyclic from of glucose (*A*)
Refer to text on page 408.

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SAMPLE QUESTION PAPER 1

A HIGHLY SIMULATED SAMPLE QUESTION PAPER FOR CBSE CLASS XII

CHEMISTRY [Fully Solved]

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Instructions

1. There are 33 questions in this question paper. All questions are compulsory.
2. **Section A :** Q. No. 1 to 16 are Objective Type Questions. Q. No. 1 and 2 are Case Based Questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
3. **Section B :** Q. No. 17 to 25 are Short answer type I questions and carry 2 marks each.
4. **Section C :** Q. No. 26 to 30 are Short answer type II questions and carry 3 marks each.
5. **Section D :** Q. No. 31 to 33 are Long answer questions carrying 5 marks each.
6. There is no overall choice. However, an internal choices have been provided.
7. Use of calculators and log tables is not permitted.

SECTION A : *Objective Questions*

Case Based Questions

1. *Read the passage given below and answer the following questions :* (1 × 4 = 4)

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to the ionic arising purely from electrostatic interactions between the metal ion and the ligand.

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal *d*-orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal *d*-orbital is directed towards the ligand than when it is away from the ligand.

Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy and the d_{xy}, d_{zx} andd_{yz} orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field.

Thus, the degeneracy of the *d*-orbitals has been removed due to ligand-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting.

The difference of energy between the two sets of degenerate orbitals as a result of crysta *l field splitting is known as* **Crystal Field Stabilisation Energy** (CFSE), it is denoted by Δ_o (the subscript *o* is for octahedral).

Thus, the energy of the two e_g orbitals will increase by (3/5) Δ_o and that of the three t_{2g} will decrease by (2/5)Δ_o.

The following questions (i-iv) are multiple choice questions. Choose the most appropriate answer :

(i) Which one of these statements about $[Co(CN)_6]^{3-}$ is correct?

(a) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a low-spin configuration.

(b) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a low-spin configuration.

(c) $[Co(CN)_6]^{3-}$ has four unpaired electrons and will be in a high-spin configuration.

(d) $[Co(CN)_6]^{3-}$ has no unpaired electrons and will be in a high-spin configuration.

(ii) Among the ligands NH_3, en, CN^- and CO, the correct order of their increasing field strength is

(a) $CO < NH_3 < en < CN^-$
(b) $NH_3 < en < CN^- < CO$
(c) $CN^- < NH_3 < CO < en$
(d) $en < CN^- < NH_3 < CO$

(iii) Identify the correct trend given below (Atomic number, Ti=22, Cr = 24 and Mo = 42)
(a) Δ_o of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$ and Δ_o of $[Ti(H_2O)_6]^{3+} < [Ti(H_2O)_6]^{2+}$
(b) Δ_o of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_o of $[Ti(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$
(c) Δ_o of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_o of $[Ti(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$
(d) Δ_o of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$ and Δ_o of $[Ti(H_2O)_6]^{3+} > [Ti(H_2O)_6]^{2+}$

Or

Crystal field stabilisation energy for high spin d^4 octahedral complex is
(a) $-0.6\Delta_o$ (b) $-1.8\Delta_o$
(c) $-1.6\Delta_o + P$ (d) $-1.2\Delta_o$

(iv) The CFSE for octahedral $[CoCl_6]^{4-}$ is 18,000 cm^{-1}. The CFSE for tetrahedral $[CoCl_4]^{2-}$ will be
(a) 18000 cm^{-1} (b) 16000 cm^{-1}
(c) 8000 cm^{-1} (d) 20000 cm^{-1}

2. *Read the passage given below and answer the following questions :* (1×4=4)

Conductivity always decreases with decrease in concentration (i.e. with dilution) of both the strong and weak electrolytes. This is due to the fact that the number of ions that carry current in a unit volume of solution always decreases with decrease in concentration.

The conductivity of a solution is the conductances of a unit volume of the solution, kept between two platinum electrodes with unit area of cross-section and at a distance of unit length, while the molar conductivity is the conductance of that volume of the solution which contains one mole of the electrolyte.

Conductivity is expressed as :

$$G = \frac{\kappa A}{l} = \kappa$$

(both A and l are unity in their appropriate units in m or cm).

While molar conductivity is expressed is $\Lambda_m = \kappa V$

It is because $\Lambda_m = \frac{\kappa A}{l}$

$\because$ $l = 1$ and $A = V$ [volume containing 1 mole of electrolyte]

Therefore, $\Lambda_m = \kappa V$

Molar conductivity increases with decrease in concentration (i.e. with dilution). This is because the total volume V of solution containing one mole of electrolyte also increases.

In these questions (i-iv) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices :

(a) Assertion and reason both are correct statements and reason is correct explanation for Assertion.
(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.
(c) Assertion is correct statement but Reason is incorrect statement.
(d) Assertion is incorrect statement but Reason is correct statement.

(i) **Assertion** Conductivity always increases with decrease in concentration for strong and weak electrolytes.

Reason Number of ions per unit volume decreases on dilution.

(ii) **Assertion** Conductivity of pure water is 3.5×10^{-5} S m^{-1}.

Reason High amounts of hydrogen ions and hydroxyl ions are present in water.

(iii) **Assertion** Conductivity of electrolytes decreases when dissolved in water.

Reason They furnish their own ions.

(iv) **Assertion** Conductivity of strong electrolytes decreases on dilution.

Reason On dilution number of ions per unit volume decreases.

Or

Assertion Λ_m for weak electrolytes shows a sharp increase, when the electrolytic solution is diluted.

Reason For weak electrolytes degree of dissociation increases with dilution of solution.

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Multiple Choice Questions

Following questions (No. 3-11) are multiple choice questions carrying 1 mark each :

3. In an alkaline medium, glycine predominantly exists as an
(a) cation (b) anion
(c) Zwitter ion (d) covalent form

4. Which of the following does not affect half-life of first order reaction?
(a) Initial concentration
(b) Catalyst
(c) Temperature
(d) Pressure

5. Identify the name of the reaction,
Bromoalkanes are prepared by refluxing the silver salts of acids with bromine in CCl_4^-.
(a) Borodine-Hunsdiecker reaction
(b) Finkelstein reaction
(c) Swarts reaction
(d) Balz-Schiemann reaction

Or

Which one undergoes S_N2 substitution reaction faster?

(a)  (b) 

(c)  (d) 

6. The standard reduction potentials of several ions are as follows

S.No.	Ions	E°
1.	Ca^{2+}	−2.87
2.	Fe^{3+}	0.77
3.	Co^{3+}	1.82
4.	Zn^{2+}	−0.76

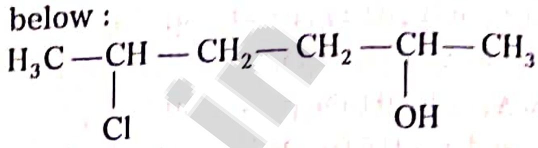
The strongest reducing agent among the following ions is
(a) Co^{3+} (b) Zn^{2+} (c) Ca^{2+} (d) Fe^{3+}

7. The coordination number of Pt in $[Pt(NH_3)_4Cl_2]^{2+}$ ion is
(a) 2 (b) 4
(c) 6 (d) 8

Or

Complex salt can be made by the combination of $[Co(NH_3)_5Cl]^x$ with
(a) Cl^- (b) $2Cl^-$
(c) PO_4^{3-} (d) $2K^+$

8. Give IUPAC name of the compound given below :



(a) 5-chlorohexan-2-ol
(b) 2-chlorohexan-5-ol
(c) 2-hydroxy-5-chlorohexane
(d) 2-chloro-5-hydroxyhexane

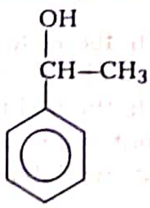
Or

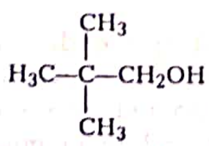
Alkenes react with water in the presence of acid as catalyst to form alcohols.

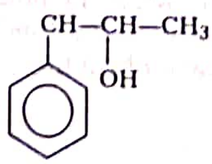
$$CH_3CH{=}CH_2 + H_2O \xrightleftharpoons{H^+} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

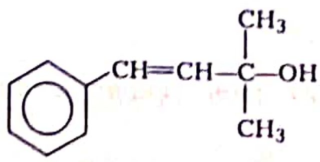
The reaction takes place in accordance with
(a) Hofmann elimination rule
(b) Saytzeff rule
(c) Markownikoff's rule
(d) Anti-Markownikoff's addition

9. Identify the primary alcohol among the given options.

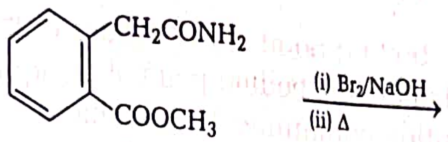
(a) 

(b) 

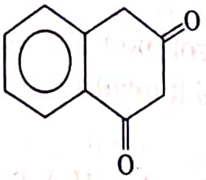
(c) 

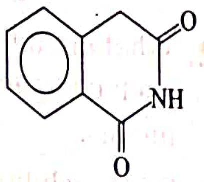
(d) 

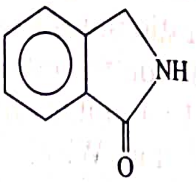
10. In the given reaction,

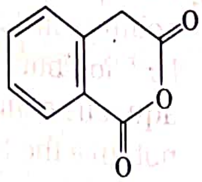


What would be the final product formed?

(a) 

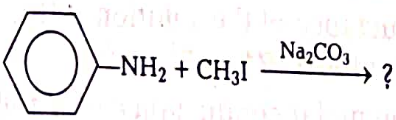
(b) 

(c) 

(d) 

Or

What is the final alkylation product in the given reaction?



(a) N, N, N-trimethylanilinium iodide
(b) N, N, N-trimethylanilinium carbonate
(c) N, N-dimethylanilinium iodide
(d) N, N-dimethylanilinium carbonate

11. Which of the following is the starting material use for the industrial preparation of phenol ?
(a) Anisole (b) Resorcinol
(c) Cumene (d) o-cresol

Assertion-Reason

In the following questions (Q.No. 12-16) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer ouf of the following choices.

(a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.
(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.
(c) Assertion is correct statement but Reason is incorrect statement.
(d) Assertion is wrong statement but Reason is correct statement.

12. **Assertion** If in a zero order reaction, the concentration of the reactant is doubled, the half-life period is also doubled.

Reason For a zero order reaction, the rate of reaction is independent of initial concentration.

13. **Assertion** pK_a value of phenol is 10.0, while that of ethanol is 15.9.

Reason Ethanol is less acidic than phenol.

Or

Assertion The density of glycerol is higher than propanol.

Reason Glycerol contain two —OH group due to which it show extensive intermolecular H-bonding.

14. **Assertion** Protein are made up of α-amino acids.

Reason During denaturation, secondary and tertiary structure of protein are destroyed.

15. **Assertion** Neopentyl chloride is formed when neopentyl alcohol reacts with HCl.

Reason Neopentyl alcohol is a primary alcohol.

16. **Assertion** S_N1 mechanism is ruled out in case of haloarene.

Reason Phenyl cation is formed as a result of self ionisation which is not stabilised by resonance.

SECTION B : *Short Answer Type I Questions*

17. Compound '*A*' on reaction with $(CH_3CO)_2O$ and NaOH gives acetanilide which on bromination gives compound '*B*' which on hydrolysis gives compound '*C*'. Identify *A*, *B* and *C*.

Or Account for the following:

(i) pK_b of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not.

18. Explain, why the melting points and solubility of amino acids in water are generally higher than that of the corresponding haloacids?

19. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

20. How will you carry out the following conversion :

(i) Aniline to benzyl alcohol

(ii) Benzene to *m*-bromophenol

21. (i) Write the effect of adding a non-volatile solute into solvent.

(ii) What is the unit of molal depression constant?

Or The boiling point of pure water is 373 K. Calculate the boiling point of an aqueous solution containing 18 g of glucose $(W=180)$ in 100 g of water. Molal elevation constant of water is 0.52 K kg mol^{-1}.

22. What are interstitial compounds? Why are such compounds well known for transition metals.

23. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. Why?

24. A solution of 0.1 N KCl offers a resistance of 245 Ω. Calculate the specific conductance and the equivalent conductance of the solution if the cell constant is 0.571 cm^{-1}.

Or Define molar conductance of a solution. State its unit. How is it related to the specific conductance of a solution?

25. The conductivity of 0.2 M KCl solution is 3×10^{-2} $ohm^{-1}cm^{-1}$. Calculate its molar condutance.

SECTION C : *Short Answer Type II Questions*

26. Define the following :

(i) Wurtz-Fittig reaction

(ii) Fittig reaction

(iii) Swarts reaction

Or

Complete the following reactions:

(i) $CH_3CH_2Cl \xrightarrow{KCN} (A) \xrightarrow{2H_2O/H^+} (B)$

(ii) $CH_3CH_2CH_2Br \xrightarrow[\Delta]{Alc.\ KOH} (A) \xrightarrow{HBr} (B)$

27. Write the balanced equations of the following reactions :

(i) Aniline and bromine water

(ii) Ethylamine and nitrous acid

(iii) Acetic anhydride and ammonia

28. (i) Give chemical tests to distinguish between the following pairs of compounds.

(a) Propanal and propanone

(b) Acetophenone and benzophenone.

(ii) Arrange the following compounds in increasing order of reactivity towards HCN.

Acetaldehyde, acetone, di- *tert*-butylketone, methyl-*tert*-butylketone.

29. (i) What is the order of following reaction?

$$N_2O_5(g) \rightleftharpoons N_2O_4(g) + \frac{1}{2}O_2(g)$$

(ii) Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law with $t_{1/2}=3$ h. What fraction of sample of sucrose remains after 8h ?

Or (i) What are pseudo first order reactions? Give one example of such reactions.

(ii) The decomposition of phosphine, PH_3 proceeds according to the following equation.

$$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$

It is found that the reaction follows the following rate equation,

$$\text{Rate} = k[PH_3]$$

The half-life of PH_3 is 37.9 s at 20°C.

(a) What fraction of original sample of PH_3 remains behind after 1 min?

(b) How much time is required of 3/4th of PH_3 to decompose?

30. Answer the following questions.

(i) Give one example of an α-amino acid.

(ii) Write the structure of the dipeptide using this example.

(iii) Write one difference between globular and fibrous proteins.

SECTION D : *Long Answer Type Questions*

31. (i) A transition metal *A* has "spin only" magnetic moment value of 1.8 BM. When it is reacted with dil. H_2SO_4 in the presence of air, a compound *B* is formed. *B* reacts with compound *C* to give compound *D* with liberation of iodine. Determine metal *A*, *B*, *C* and *D*.

(ii) Describe the cause of the following variation:

(a) Zn, Cd and Hg normally not regarded as transition elements.

(b) Compounds of transition metals are coloured.

(c) Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state.

Or

(i) What happens when, Europium shows +2 oxidation state.

(ii) Explain the following:

(a) Among d^4 species, Cr^{2+} is strongly reducing while Mn (III) is strongly oxidising.

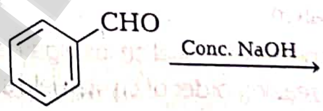
(b) Cobalt (II) is stable in an aqueous solution but in the presence of complexing reagents it is easily oxidised.

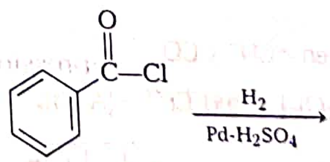
(c) The d^1-configuration is very unstable in ions.

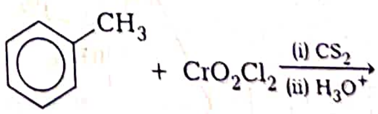
32. An organic compound *A* on treatment with acetic acid in the presence of sulphuric acid produces an ester *B*. *A* on mild oxidation gives *C*. *C* with 50% KOH followed by acidification with dil. HCl generates *A* and *D*. *D* with PCl_5 followed by reaction with NH_3 gives *E*, which on dehydration produces HCN. Identify *A* to *E*.

Or Complete the following reactions :

(i) $2H-\underset{\underset{O}{\|}}{C}-H \xrightarrow{\text{Conc. KOH}}$

(ii) 

(iii) 

(iv) 

(v) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2}$

33. (i) 1000 g of 1 molal aqueous solution of sucrose is cooled and maintained at −3.534° C. Calculate the ice that will separate out at this temperature.

(ii) The solubility of $Ba(OH)_2 \cdot 8H_2O$ in H_2O is 5.6 g per 100 g of H_2O at 288 K. Calculate the molality of hydroxide ion in saturated solution of $Ba(OH)_2 \cdot 8H_2O$ at that temperature.

Or A solution containing 30 g of a non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9kPa at 298K. Calculate

(i) molar mass of the solute

(ii) vapour pressure of water at 298 K.

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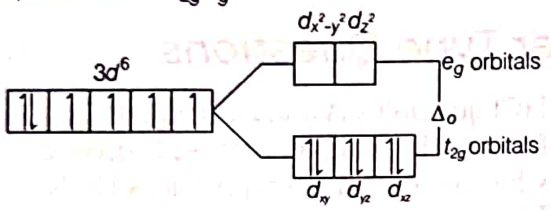
Solutions

1. (i) (a) Statement (a) is correct. $[Co(CN)_6]^{3-}$

$Co^{3+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6$

CN^- is a strong field ligand and as it approaches the metal ion, the electron must pair up.

The splitting of the *d*-orbitals into two sets of orbitals in an octahedral complex $[Co(CN)_6]^{3-}$ may be represented as $t_{2g}^6 e_g^0$.



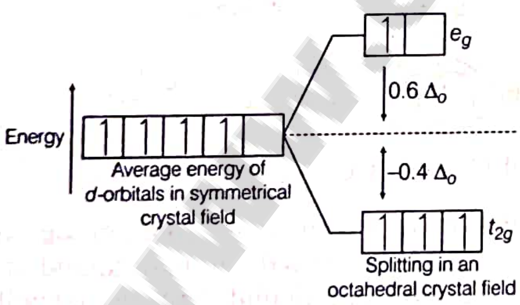
Here, for d^6 ions, three electrons first inner orbitals with parallel spin out the remaining may pair up in t_{2g} orbital giving rise to low spin complex (strong ligand) field.

$\therefore$ $[Co(CN)_6]^{3-}$ has no unpaired electron and will be in low spin configuration. **(1)**

(ii) (b) Based on spectrochemical series, ligands arranged in increasing order of crystal field strength are as **(1)**

$$NH_3 < en < CN^- < CO$$

(iii) (b) For $[Cr(H_2O)_6]^{2+}$ and $Cr^{2+} = [Ar], 3d^4$



(1)

As H_2O is a weak field ligand, so pairing of electrons does not occur.

CFSE for $[Cr(H_2O)_6]^{2+} = 3(-0.4\Delta_o) + 1(0.6\Delta_o) = -0.6\Delta_o$

$\Delta_o \propto$ Crystal Field Stabilisation Energy (CFSE)

Δ_o depends on Z_{eff} and for 3*d*-series, Z_{eff} is less than 4*d* -series.

Hence, Δ_o of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$

From above table,

Δ_o of $[Ti(H_2O)_6]^{3+} > \Delta_o$ of $[Ti(H_2O)_6]^{2+}$

Or

(a) $CFSE = 3(-0.4) + 1(0.6) = -0.6\Delta_o$

(iv) (c) CFSE for octahedral and tetrahedral complexes are closely related to each other by formula $\Delta_t = \frac{4}{9}\Delta_o$.

where, Δ_o = CFSE for octahedral complex,
Δ_t = CFSE for tetrahedral complex

According to question, $\Delta_o = 18000\ cm^{-1}$

$$\therefore \quad \Delta_t = \frac{4}{9}\Delta_o = \frac{4}{9} \times 18000\ cm^{-1}$$
$$= 4 \times 2000\ cm^{-1} = 8000\ cm^{-1}$$

Hence, correct choice is option (c). **(1)**

2. (i) (d) Conductivity always decreases with decrease in concentration for weak and strong electrolytes. This is explained by the decrease in the number of ions per unit volume that carry current in solution on dilution. Hence, Assertion is incorrect but Reason is correct. **(1)**

(ii) (c) Pure water has small amounts of hydrogen and hydroxyl ions ($\sim 10^{-7}$ M) due to which it has very low conductivity ($3.5 \times 10^{-5}\ S\ m^{-1}$). **(1)**

Hence, Assertion is correct but Reason is incorrect.

(iii) (d) When electrolytes are dissolved in water, they furnish their own ions in the solution, hence the conductivity increases. **(1)**

Hence, Assertion is incorrect but Reason is correct.

(iv) (a) Since, conductivity depends upon the number of ions per unit volume. Therefore, the conductivity of strong electrolytes decreases on dilution due to decrease in number of ions per unit volume.

Hence, both Assertion and Reason are correct but Reason is the correct explanation of Assertion. **(1)**

Or

(a) Molar conductivity of weak electrolytic solution increases on dilution because as we add excess water to increase the dilution, degree of dissociation increases which leads to increase in the number of ions in the solution. Thus, Λ_m show a very sharp increase.

Hence, both Assertion and Reason are correct but Reason is the correct explanation of Assertion. **(1)**

3. (b) In alkaline medium, glycine predominantly exists as an anion. It is shown as follows

$$H_3N^+{-}CH_2{-}COO^- + OH^- \longrightarrow H_2\ddot{N}{-}CH_2{-}CO\bar{O} + H_2O$$

4. (a) $t_{1/2} = \frac{0.0693}{k}$ for first order reaction. So, it is **(1)**
independent of initial concentration. **(1)**

5. (a) Generally, bromoalkanes are prepared by refluxing the silver salts of acids with bromine in CCl_4.

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This reaction is known as Borodine-Hunsdiecker reaction. The reaction can be depicted as

$$\underset{\text{Silver salt of acid}}{CH_3COO^-Ag^+} + Br_2 \xrightarrow{CCl_4} \underset{\text{Methyl bromide}}{CH_3Br} + \underset{\text{Carbon-dioxide}}{CO_2\uparrow} + \underset{\text{Silver bromide}}{AgBr} \quad (1)$$

Or

(a)  undergoes S_N2 reaction faster due to low C—I bond dissociation energy.

6. (c) Ca^{2+} is the strongest reducing agent as its value of reduction potential is the lowest. (1)

7. (c) 6

Or

Let x be the coordination number of given complex ion be x.

$$\therefore \quad x = [3 + 5(-3 + 3\times(+1) + (-1))]$$
$$= +2$$

Thus, complex salt would be $[Co(NH_3)_5Cl]Cl_2$. (1)

8. (a) 5-chlorohexan-2-ol is the IUPAC name of given compound.

$$\overset{6}{H_3C}-\underset{\underset{Cl}{|}}{\overset{5}{CH}}-\overset{4}{CH_2}-\overset{3}{CH_2}-\underset{\underset{OH}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$$ (1)

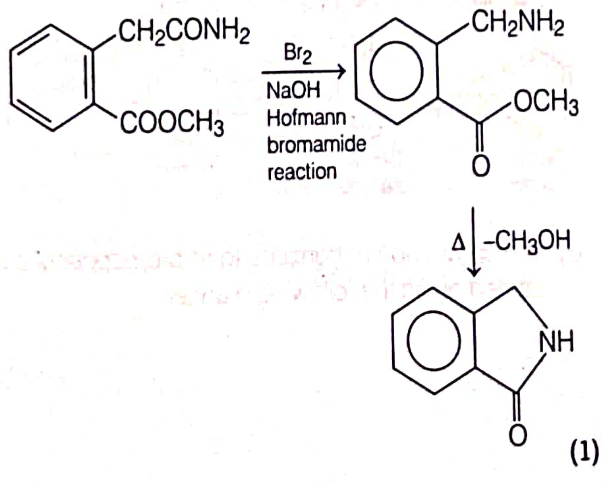
Or

(c) Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markownikoff's rule.

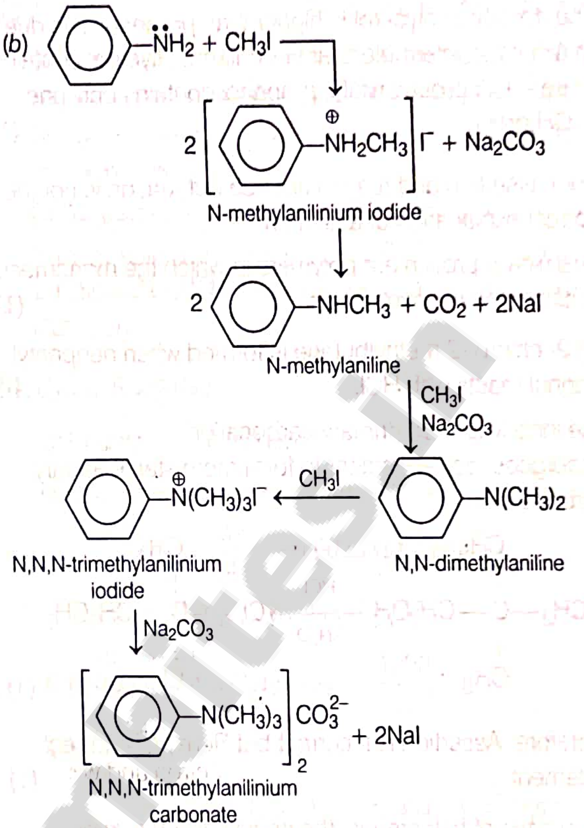
$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2O \underset{}{\overset{H^{\oplus}}{\rightleftharpoons}} \underset{\text{Propan-2-ol}}{H_3C-\underset{\underset{OH}{|}}{CH}-CH_3}$$ (1)

9. (b) Primary alcohols contain $-CH_2OH$ group.

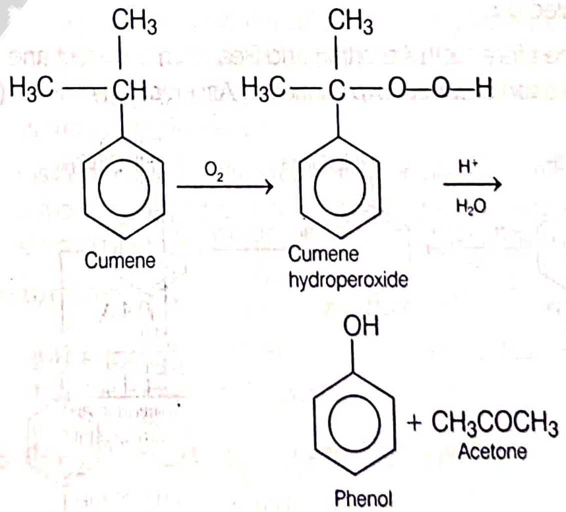
So, $H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH$ is a primary alcohol. (1)

10. (c)  (1)

Or

(b)  (1)

11. (c) The starting material used for the industrial preparation of phenol is cumene.

 (1)

12. (b) Both assertion and reason are true but reason is not the correct explanation of assertion.

For a zero order reaction, $t_{1/2} = \frac{[A_0]}{2k}$. (1)

13. (a) Both assertion and reason are true and reason is the correct explanation of assertion.

Ethanol is less acidic than phenol as phenoxide ion formed after loosing H^+ ion is more stable due to resonance. (1)

Or

Assertion is true but reason is false.

Correct reason is as follows

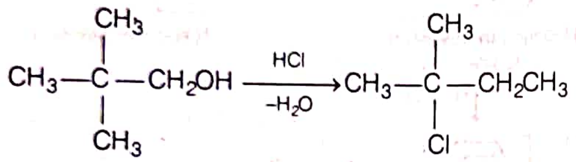
The density of glycerol is higher than propanol, it is due to extensive intermolecular H-bonding. Glycerol contains three —OH groups while, propanol contains only one —OH group. (1)

14. Both assertion and reason are true but reason is not the correct explanation of assertion.

Chemically protein are polymers in which the monomeric units are the α-amino acids. (1)

15. (*d*) 2- chloro -2 methylbutane is formed when neopentyl alcohol reacts with HCl.

The initially formed primary carbocation undergoes rearrangement to form more stable tertiary carbocation.



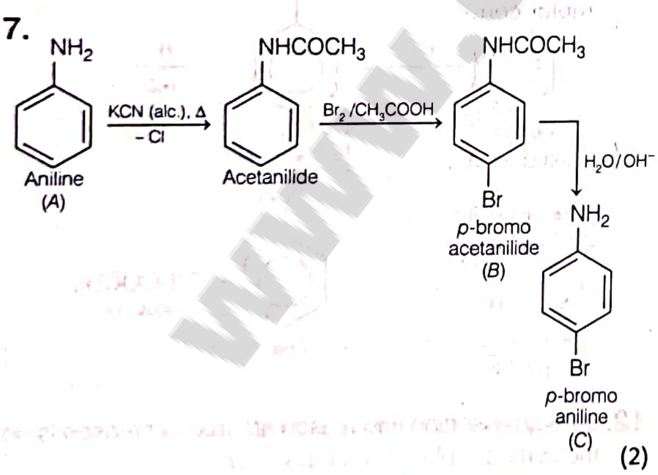
(1)

Therefore, Assertion is incorrect but Reason is correct statement. (1)

16. (*a*) In case of haloarenes, the phenyl cation formed as a result of self ionisation will not be stabilised by resonance and therefore S_N1 mechanism is ruled out.

Therefore, both Assertion and Reason are correct and Reason is correct explanation of Assertion. (1)

17.

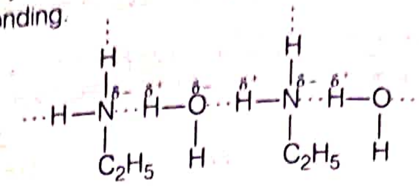


(2)

Or (i) In aniline, the electron pair on nitrogen atom is involved in conjugation with ring and is less available for protonation than that in methylamine.

Therefore, pK_b value of aniline is more than that of methylamine and aniline is less basic (as higher the pK_b value, weaker is the base). (1)

(ii) Ethylamine is soluble in water due to hydrogen bonding.



In aniline due to bulky hydrocarbon part, the extent of hydrogen bonding is less and it is not soluble in water. (1)

18. The amino acids exists as *Zwitter* ions in aqueous solution. Due to this, dipolar salt like structure amino acids have strong dipole-dipole interactions.

Thus, their melting points are higher than corresponding haloacid which do not have salt like character. Secondly, they interact strongly with H_2O due to their salt like character. As a result, polar amino acids dissolve in polar solvents like H_2O. (2)

19. Let $a = 100, a - x = 100 - 30 = 70, t = 40$ min

For first order reaction,

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)} = \frac{2.303}{40 \text{ min}}\log\frac{100}{70}$$

$$= \frac{2.303}{40}\log\frac{10}{7} = \frac{2.303}{40}\log 1.428$$

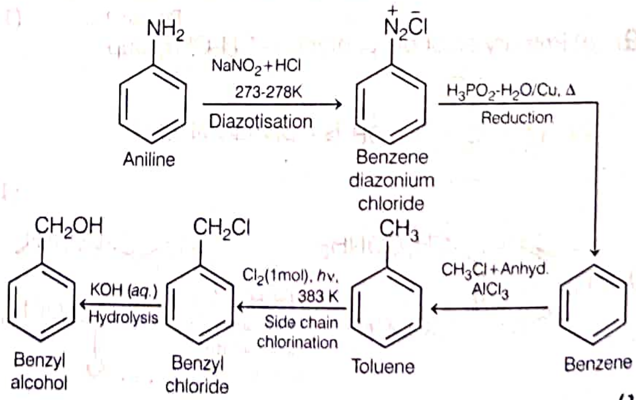
$$= \frac{2.303}{40}\times 0.1548$$

$$k = 8.91\times 10^{-3}\text{ min}^{-1}$$

Also, $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.91\times 10^{-3}\text{ min}^{-1}} = 77.78 \text{ min}$$

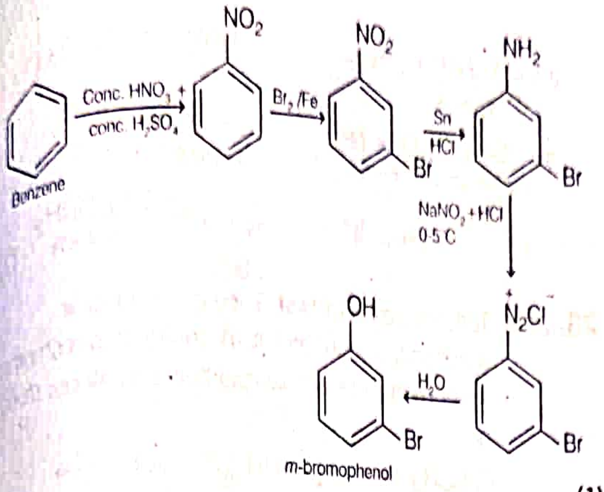
$$t_{1/2} = 77.78 \text{ min}$$ (2)

20. (i) The conversion of aniline into benzyl alcohol can be carried out in the following manner



(1)

(ii) The conversion of benzene to *m*-bromophenol can be carried out in the following manner



(1)

21. (i) The effect of adding a non-volatile solute to a solvent is to

- lower the vapour pressure
- lower the freezing point
- increases the boiling point
- increases the osmotic pressure (1)

(ii) The unit of molal depression constant is $K\,kg\,mol^{-1}$. (1)

Or

Given, boiling point of pure water = 373 K

Weight of solute, $w = 18\,g$,

Weight of solvent, $W = 100\,g$,

Molecular weight of solute, $m = 180\ g\ mol^{-1}$ (1)

K_b for water = $0.52\,K\,kg\,mol^{-1}$

For glucose as solute $i = 1$

$$\therefore \quad \Delta T_b = \frac{1000 \times K_b \times w}{m \times W}$$

$$= \frac{1000 \times 0.52 \times 18}{180 \times 100} = 0.52\,K$$

$\therefore$ Boiling point of solution $= T_b + \Delta T_b$

(where, T_b is boiling point of water $= 100°C = 373\,K$)

$= 373 + 0.52 = 373.52\,K$ (1)

22. The compounds in which small atoms like H, C, N, etc. occupy interstitial sites in the crystal lattice are called interstitial compounds. These compounds are well known for transition metals because small atoms can easily occupy the position in the voids present in the crystal lattices of transition metals. (2)

23. When $FeSO_4$ and $(NH_4)_2SO_4$ solution are mixed in 1:1 molar ratio, Mohr's salt (a double salt) is formed.

$$FeSO_4(aq) + (NH_4)_2SO_4(aq) \longrightarrow FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$$

$$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \rightleftharpoons Fe^{2+}(aq) + 2NH_4^+(aq) + 2SO_4^{2-}(aq) + 6H_2O$$

Because Fe^{2+} ions are formed on dissolution of Mohr's salt, its aqueous solution gives the test of Fe^{2+} ions.

But when $CuSO_4$ is mixed with ammonia, following reaction occurs,

$$CuSO_4(aq) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]SO_4$$

This complex does not produce Cu^{2+} ion, so the solution of $CuSO_4$ and NH_3 does not give the test of Cu^{2+} ion. (1)

24. Given, $R = 245\Omega$,

Cell constant $= 0.571\,cm^{-1}$

Hence, specific conductance $= G/R$

$$\kappa = \frac{0.571}{245} = 0.00233\,\Omega^{-1}\,cm^{-1}$$

$$= 2.33 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$$ (1)

Equivalent conductance $\Lambda_{eq} = \frac{1000}{C} \times \kappa$

Concentration, $C = 0.1\,N$

$$\Lambda_{eq} = \frac{1000}{0.1} \times 2.33 \times 10^{-3} = 23.3\,\Omega^{-1}\,cm^2\,equiv^{-1}$$ (1)

Or

The conductance of that volume of solution which contains one mole of the solute and is placed between two parallel electrode of 1 cm distance apart and having sufficient area to hold the whole of the solution is called its **molar conductance**. (1)

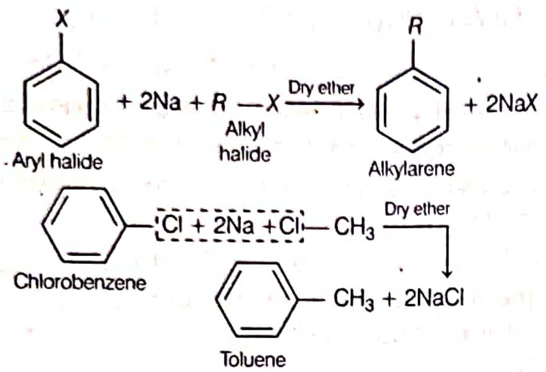
It is denoted by Λ_m. If the concentration of a solution is C mol/L, then volume of the solution containing 1 mole of the electrolyte will be 1/C L or 1000/C cc. Hence, Λ_m and κ can be related as $\Lambda_m = \frac{1000}{C} \times \kappa$, where κ is specific conductance. Its units are $ohm^{-1}\,cm^2\,mol^{-1}$ in CGS and $ohm^{-1}\,m^2\,mol^{-1}$ in SI system. (1)

25. Given, $C = 0.2\,M$, $\Lambda_{sp} = 3 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$

Putting value, $\Lambda_m = \frac{1000}{0.2} \times 3 \times 10^{-2}$

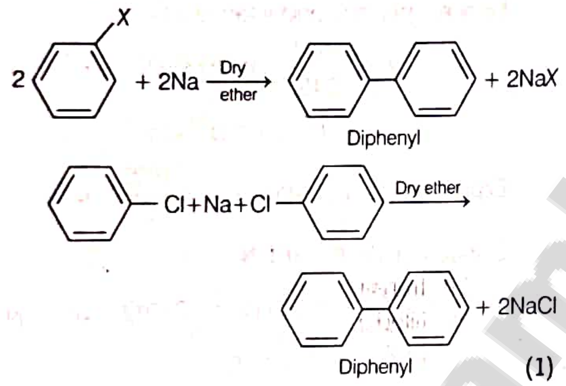
$$= \frac{30}{0.2} = 1.5 \times 10^2\,\Omega^{-1}\,cm^2\,mol^{-1}$$ (2)

26. (i) **Wurtz-Fittig reaction** When aryl halide is heated with alkyl halide in the presence of sodium in dry ether, halogen atom is replaced by alkyl group and alkylarene is formed. This reaction is called Wurtz-Fittig reaction.



(1)

(ii) **Fittig reaction** When haloarenes react with sodium in the presence of dry ether, two aryl groups are joined together and diphenyl is formed. This reaction is called Fittig reaction.



(1)

(iii) **Swarts reaction** The synthesis of alkyl fluorides is achieved by heating an alkyl bromide/chloride in the presence of AgF, Hg_2F_2, CoF_2 or SbF_3. This reaction is known as Swarts reaction.

$R—Br + AgF \longrightarrow R—F + AgBr$

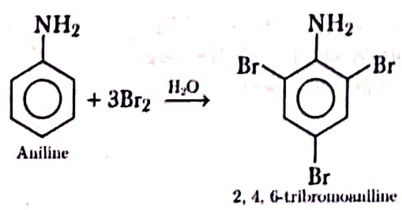
$H_3C—Br + AgF \longrightarrow H_3C—F + AgBr$ (1)

Or

(i) $\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow{KCN} \underset{\substack{\text{Ethyl nitrile}\\(A)}}{CH_3CH_2CN} \xrightarrow{2H_2O/H^+} \underset{\substack{\text{Propanoic acid}\\(B)}}{CH_3CH_2COOH}$ (1/2)

(ii) $\underset{\text{1- bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\Delta]{\text{Alc.KOH}} \underset{\substack{\text{Prop-1-ene}\\(A)}}{CH_3CH=CH_2} \xrightarrow{HBr} \underset{\substack{\text{2-bromopropane}\\(B)}}{CH_3\underset{\underset{Br}{|}}{C}H—CH_3}$ (1½)

27. (i)



(ii) $\underset{\text{Ethylamine}}{C_2H_5NH_2} + HNO_2 \longrightarrow \underset{\text{Ethanol}}{C_2H_5OH} + N_2\uparrow + H_2O$

(iii) $\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + NH_3 \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Acetamide}}{CH_3CONH_2}$ (3)

28. (i) (a) **Tollen's reagent test** Since propanal is an aldehyde, it reduces Tollen's reagent to a shining silver mirror but propanone being a ketone, does not.

$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + \underset{\text{Silver mirror}}{2Ag}\downarrow + 4NH_3 + 2H_2O$

$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow{\text{Tollen's reagent}} \text{No silver mirror}$ (1)

(b) **Iodoform test** Acetophenone being a methylketone on treatment with NaOI (I_2/NaOH) gives yellow precipitate of iodoform but benzophenone does not.

$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3NaOI \longrightarrow C_6H_5COONa + \underset{\text{Iodoform}}{CHI_3}\downarrow + 2NaOH$

$\underset{\text{Benzophenone}}{C_6H_5COC_6H_5} \xrightarrow{NaOI} \text{No ppt.}$ (1)

(ii) The reactivity towards HCN addition decreases as +*I*-effect of the alkyl group increases. Therefore, the correct order of reactivity is :

Di-*tert*-butyl ketone < *tert*-butylmethyl ketone < acetone < acetaldehyde. (1)

29. (i) The order of given reaction is one. (1)

(ii) For first order reactions, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(3.0\text{ h})}$

or $t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$

or $\log\frac{[A]_0}{[A]} = \frac{k \times t}{2.303}$

$\log\frac{[A]_0}{[A]} = \frac{0.693}{3\text{ h}} \times \frac{8\text{ h}}{2.303} = 0.8024$

$\frac{[A]_0}{[A]} = \text{antilog } 0.8024 = 6.345$ (1)

$[A]_0 = 1\text{M};$

$[A] = \frac{[A]_0}{6.345} = \frac{1\text{ M}}{6.345} = 0.1576\text{M}$

After 8 h, sucrose left = 0.1576 M (1)

Or (i) **Pseudo first order reaction** The reaction which is bimolecular but has order one, is called pseudo first order reaction, e.g. acidic hydrolysis of ester.

$CH_3COOC_2H_5 + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOH + C_2H_5OH$ (1)

(ii) Given, $t_{1/2} = 37.9$ s

Initial concentration $= [R]_0$

Concentration after time, $t = \dfrac{[R]_0}{4}$

[because 3/4th of the PH_3 is decomposed]

(a) $t = 1$ min $= 60$ s

$$k = \frac{0.693}{37.9} = 0.0183\,\text{s}^{-1}$$

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}$$

$$60 = \frac{2.303}{0.0183}\log\frac{[R]_0}{[R]}$$

or $\log\dfrac{[R]_0}{[R]} = \dfrac{60 \times 0.0183}{2.303} = 0.4768$

$$\frac{[R]_0}{[R]} = \text{antilog } 0.4768 \Rightarrow \frac{[R]_0}{[R]} = 2.997$$

Let the initial amount $[R_0]$ is 100

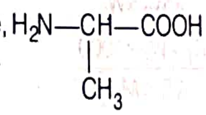
$$\frac{100}{2.997} = [R]$$

$$[R] = 33.3\%$$ (1)

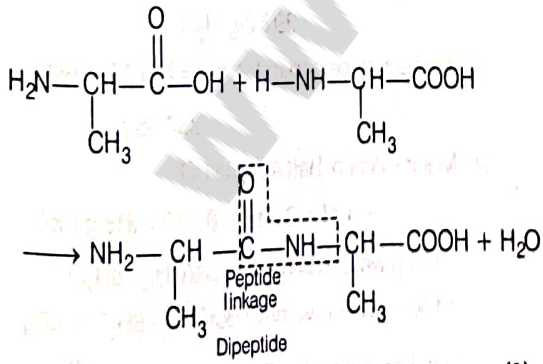
(b) $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{37.9}\,\text{s}^{-1}$

$$t = \frac{2.303}{k}\log\frac{[R]_0}{\left[\frac{[R]_0}{4}\right]} = \frac{2.303}{\frac{0.693}{37.9}}\log 4$$

$$t = \frac{2.303 \times 37.9 \times 0.6020}{0.693} = 75.82\text{ s}$$ (1)

30. (i) Alanine, 

(ii) When two α-amino acids combine, a dipeptide is formed with the loss of a water molecule.



(1)

(iii) • **Fibrous proteins** They have thread or fibre like structures in which polypeptide chains run parallel. These proteins are insoluble in water, e.g. keratin (found in hair, skin, nails, wool, silk) and myosin (present in muscles).

• **Globular proteins** They have spherical shape in which chains of polypeptides coil around. These are soluble in water, e.g. insulin and albumins. (1)

31. (i) The spin only magnetic moment is given by

$$\mu = \sqrt{n(n+2)}$$

Thus, $\sqrt{n(n+2)} = 1.8$

Squaring both sides,

$$n(n+2) = 3.24$$
$$n^2 + 2n = 3$$
$$n^2 + 2n - 3 = 0$$
$$n^2 + 3n - n - 3 = 0$$
$$(n-1)(n+3) = 0$$

$\Rightarrow n = 1$, but $n \neq -3$ is not possible.

Thus, $n = 1$

It means that one unpaired electron is present. i.e. it is copper.

Thus, $\underset{(A)}{2Cu} + 2H_2SO_4 + O_2 \longrightarrow \underset{(B)}{2CuSO_4} + 2H_2O$

$$\underset{(B)}{2CuSO_4} + \underset{(C)}{4KI} \longrightarrow 2K_2SO_4 + 2CuI_2$$

$$2CuI_2 \longrightarrow \underset{(D)}{Cu_2I_2} + I_2$$

(2)

(ii) (a) Transition elements are those which, have partly filled d-orbitals. Since, neither the atoms nor ions of Zn, Cd and Hg have partly filled d-orbitals, they are normally not regarded as transition metals. (1)

(b) Compounds of transition metals are coloured due to d-d transition. (1)

(c) Electronic configuration of Mn^{2+} is $3d^5$ which is half-filled and hence stable. So, 3rd ionisation enthalpy is very high, i.e. 3rd electron cannot be lost easily. In case of Fe^{2+}, electronic configuration is $3d^6$. Thus, it can lose one electron easily to give the stable configuration $3d^5$. (1)

Or

(i) Europium in + 2 oxidation state shows stable electronic configuration, i.e. $[Xe]4f^7 5d^0 6s^0$. (2)

(ii) (a) E values for Cr^{3+}/Cr^{2+} is negative (−0.41) and for Mn^{3+}/Mn^{2+} is positive (+1.57 V). Thus, Cr^{2+} can undergo oxidation and therefore, acts as a reducing agent. On the other hand, Mn (III) can undergo reduction, and therefore, it acts as an oxidising agent. (1)

(b) In the presence of complexing agents, cobalt gets oxidised from +2 to +3 state because Co (III) is more stable than Co (II) (1)

(c) After loss of ns electrons d^1-electron can easily be lost to give a stable configuration. Therefore, the elements having d^1 configuration are either reducing or undergo disproportionation. (1)

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32. $A \xrightarrow[(H_2SO_4)]{CH_3COOH} \underset{\text{Ester}}{B}$

Thus, A is an alcohol.

$$A \xrightarrow{\text{Mild oxidation}} C \xrightarrow[\text{Dil. HCl}]{50\%\ KOH} \underset{\text{Alcohol}}{A} + \underset{\text{Acid}}{D}$$

Thus, C undergoes Cannizzaro reaction.

$$D \xrightarrow{PCl_5} \xrightarrow{NH_3} E \xrightarrow[-H_2O]{} HCN$$

Thus, E is $H-\overset{O}{\overset{\|}{C}}-NH_2$, because on dehydration, it gives HCN (with intermediate HCOCl).

D is $H-\overset{O}{\overset{\|}{C}}-OH$ (because only $H-\overset{O}{\overset{\|}{C}}-OH$ gives E when it reacts with PCl_5 and NH_3). C is HCHO, as C gives Cannizzaro reaction in the presence of KOH and forms alcohol and salt of carboxylic acid, A is CH_3OH. Because C is only formed by oxidation of CH_3OH.

$$B \text{ is } CH_3-\overset{O}{\overset{\|}{C}}-OCH_3 \qquad (3)$$

The reactions involved are

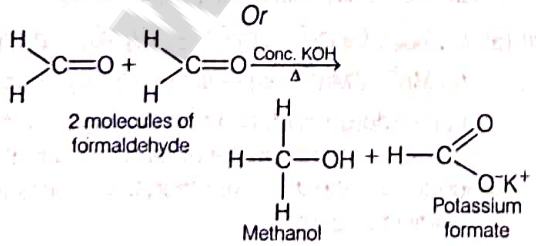
$$\underset{\text{(Acetic acid)}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + \underset{\underset{(A)}{\text{Methanol}}}{CH_3OH} \xrightarrow{H_2SO_4} \underset{\underset{\text{Methyl acetate}}{(B)}}{CH_3-\overset{O}{\overset{\|}{C}}-OCH_3}$$

$$\underset{(A)}{CH_3OH} \xrightarrow{\text{Mild oxidation}} \underset{(C)}{HCHO}$$

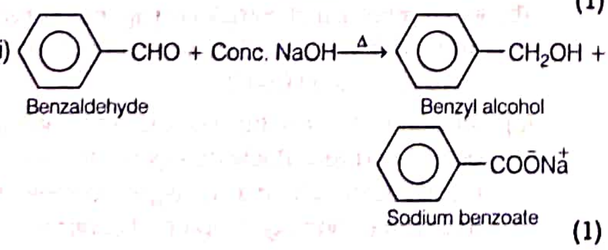
$$\underset{(C)}{HCHO} \xrightarrow[\text{Dil.HCl}]{KOH} \underset{(D)}{HCOOH} + \underset{\underset{(A)}{\text{Formaldehyde}}}{CH_3OH}$$

$$\underset{\underset{(D)}{\text{Methanoic acid}}}{HCOOH} \xrightarrow{PCl_5} H-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[-HCl]{NH_3} \underset{(E)}{H-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow[-H_2O]{\Delta} HCN \qquad (2)$$

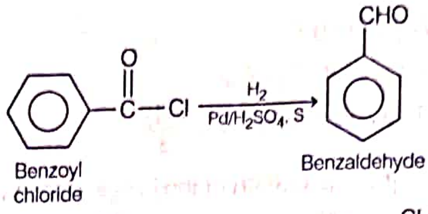
Or

(i) 

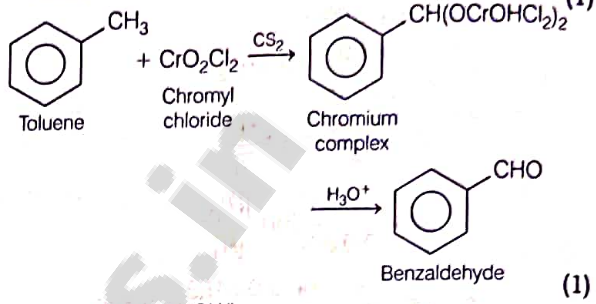
(1)

(ii) 

(1)

(iii) 

(1)

(iv) 

(1)

(v) $\underset{\text{Acetophenone}}{C_6H_5COCH_3} \xrightarrow{NaOH/I_2} C_6H_5COO^-Na^+ + \underset{\text{Iodoform}}{CHI_3\downarrow}$ (1)

33. (i) 1 m = 342 g per 1000 g of H_2O

Sugar in 1000 g of solution is

1342 g solution ≡ 342 g sugar

$$1000 \text{ g solution} = \frac{342 \times 1000}{1342} = 254.85 \text{ g}$$

Mass of H_2O per 1000 g solution

$$= 1000 - 254.85$$
$$= 745.15 \text{ g}$$

$$\Delta T_f = \frac{K_f \times 1000 \times \text{grams of sucrose}}{Mw_{sugar} \times \text{grams of } H_2O \text{ left}}$$

$$= \frac{K_f \times W_2 \times 1000}{Mw_2 \times W_1}$$

$$W_1 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times Mw_2}$$

$$= \frac{1.86 \times 254.84 \times 1000}{3.534 \times 342}$$

$$= 392.2 \text{ g } H_2O$$

Amount of ice separates out = 745.15 − 392.2

≡ 352.95 g (2½)

(ii) Molar mass of $Ba(OH)_2 \cdot 8H_2O$

$$= 137 + 2 \times 17 + 8 \times 18 = 315 \text{ g mol}^{-1}$$

∴ 100 g water has 5.6 g of $Ba(OH)_2 \cdot 8H_2O$

∴ 1000 g water will have $Ba(OH)_2 \cdot 8H_2O$ = 56g

$$\text{Number of moles of } Ba(OH)_2 \cdot 8H_2O = \frac{56}{315}$$
$$= 0.178 \text{ mol}$$

Thus, molality of $Ba(OH)_2$ = 0.178 m

$$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$$

Molality of OH^- ions = 2 × molality of $Ba(OH)_2$

$$= 2 \times 0.178$$
$$= 0.356 \text{ m} \qquad (2½)$$

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Or (i) Suppose, the molar mass of solute = M g mol^{-1}

Number of moles of solute $(n_2) = \frac{30}{M}$ mol

Number of moles of H_2O

$$(n_1) = \frac{90\text{ g}}{18\text{ g mol}^{-1}} = 5\text{ mol}$$

$$p_1 = 2.8\text{ kPa}$$

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{n_2}{n_1 + n_2}$$

$$\Rightarrow \frac{p_1^\circ - 2.8}{p_1^\circ} = \frac{30/M}{5 + 30/M}$$ **(1)**

or $$1 - \frac{2.8}{p_1^\circ} = \frac{30/M}{5 + 30/M}$$

or $$\frac{2.8}{p_1^\circ} = 1 - \frac{30/M}{5 + 30/M} = \frac{5}{5 + 30/M}$$

or $$\frac{p_1^\circ}{2.8} = \frac{5 + 30/M}{5} = 1 + \frac{6}{M} \quad \text{...(i)}$$ **(1)**

On adding 18 g of water, $n(H_2O) = 6$ mol

(= 5 + 1 = 6 mol)

Then, $p_1' = 2.9$ kPa

$$\therefore \frac{p_1^\circ - 2.9}{p_1^\circ} = \frac{30/M}{6 + 30/M}$$

or $$1 - \frac{2.9}{p_1^\circ} = \frac{30/M}{6 + 30/M}$$

or $$\frac{2.9}{p_1^\circ} = 1 - \frac{30/M}{6 + 30/M}$$

$$= \frac{6}{6 + 30/M}$$

or $$\frac{p_1^\circ}{2.9} = \frac{6 + 30/M}{6} = 1 + \frac{5}{M} \quad \text{...(ii)}$$ **(1)**

On dividing Eq. (i) by Eq. (ii), we get

$$\frac{2.9}{2.8} = \frac{1 + 6/M}{1 + 5/M}$$

or $$2.9\left(1 + \frac{5}{M}\right) = 2.8\left(1 + \frac{6}{M}\right)$$

or $$2.9 + \frac{14.5}{M} = 2.8 + \frac{16.8}{M} \Rightarrow M = 23\text{ u}$$ **(1)**

(ii) Putting, $M = 23$ in Eq. (i), we get

$$\frac{p_1^\circ}{2.8} = 1 + \frac{6}{23} = \frac{29}{23}$$

or $$p_1^\circ = \frac{29}{23} \times 2.8 = 3.53\text{ kPa}$$ **(1)**

FULLY SO

SAMPLE QUESTION PAPER 2

A HIGHLY SIMULATED SAMPLE QUESTION PAPER FOR CBSE CLASS XII

CHEMISTRY [Fully Solved]

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Instructions

1. There are 33 questions in this question paper. All questions are compulsory.
2. **Section A :** Q. No. 1 to 16 are Objective Type Questions. Q. No. 1 and 2 are Case Based Questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
3. **Section B :** Q. No. 17 to 25 are Short answer type I questions and carry 2 marks each.
4. **Section C :** Q. No. 26 to 30 are Short answer type II questions and carry 3 marks each.
5. **Section D :** Q. No. 31 to 33 are Long answer questions carrying 5 marks each.
6. There is no overall choice. However, an internal choices have been provided.
7. Use of calculators and log tables is not permitted.

SECTION A : *Objective Questions*

Case Based Questions

1. *Read the passage given below and answer the following questions :* (1×4=4)

Molar conductivity of a solution is the conductance of solution containing one mole of electrolyte, kept between two electrodes having unit length between them and large cross-sectional area, so as to contain the electrolyte.

In other words, molar conductivity is the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross-section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. It is denoted by Λ_m.

By knowing molar concentration (C) and conductivity (κ), Λ_m can be calculated.

Λ_m° is called molar conductivity at infinite dilution.

The molar conductivity of strong electrolytes is found to vary with concentration according to the Debye-Huckel Onsager equation.

In that equation, A is constant depending upon the type of electrolyte taken and nature of **solvent** and **temperature.**

The following questions (i-iv) are multiple choice questions. Choose the most appropriate answer :

(i) If conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}, the molar conductivity of the solution shall be (in S cm^{2}mol^{-1})

(a) 3.276 (b) 0.3276
(c) 32.76 (d) 327.6

(ii) Molar conductivity of a solution is $126 \times 10^2 \Omega^{-1}cm^2mol^{-1}$. Its molarity is 0.01. Its specific conductivity will be

(a) 1.26×10^{-5} (b) 1.26×10^{-3}
(c) 1.26×10^{-4} (d) 12.6×10^{-3} (1)

(iii) The increase in molar conductivity of HCl with dilution is due to

(a) increase in self-ionisation of water
(b) hydrolysis of HCl
(c) decrease in self-ionisation of water
(d) decrease in interionic forces (1)

Or

Highest molar conductivity will be exhibited by

(a) 0.005 M NaCl (b) 0.1 M NaCl
(c) 0.5 M NaCl (d) 0.01 M NaCl

(iv) Which of the following is wrong about molar conductivity ?

(a) The solution contains Avogadro number of molecules of the electrolyte.

(b) It is the product of specific conductivity and volume of solution in cc containing 1 mole of electrolyte.

(c) Its unit is $ohm^{-1}\ cm^2 mol^{-1}$

(d) Its value for 1 M NaCl is same as that of 1 M glucose solution..

2. *Read the passage given below and answer the following questions :* (1×4=4)

Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light. Many volatile halogen compounds have sweet smell.

Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are gases at room temperature. Higher member are liquids or solids. As we have already learnt, molecules of organic halogen compounds are generally polar. Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals' are stronger in the halogen derivatives. That is why the boiling point of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.

Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water. The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms.

The haloalkanes are only very slightly soluble in water. In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is release when new attractions are setup between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water.

In these questions (i-iv) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices :

(a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.

(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.

(c) Assertion is correct statement but Reason is incorrect statement.

(d) Assertion is incorrect statement but Reason is correct statement.

(i) **Assertion** Boiling point of alkyl halides increases with increase in molecular weight.

Reason Boiling point of alkyl halides are in the order $RI > RBr > RCl > RF$.

(ii) **Assertion** Alkyl halides are soluble in organic solvents.

Reason *p*-dichlorobenzene possesses low melting point.

(iii) **Assertion** Lower members of alkyl halides are colourless gases.

Reason Alkyl halides in general turn black.

Or

Assertion Haloalkanes does not show H-bonding.

Reason Haloalkanes are soluble in water.

(iv) **Assertion** Fluoride has the lowest and iodide has the highest boiling point.

Reason Boiling points of haloalkanes increases with increasing atomic mass.

Multiple Choice Questions

Following questions (No. 3-11) are multiple choice questions carrying 1 mark each :

3. It is true that

(a) a second order reaction is always a multistep reaction.

(b) a zero order reaction is a multistep reaction

(c) a first order reaction is always a single step reaction

(d) a zero order reaction is a single step reaction

Or

A reaction involving two different reactants can never be

(a) bimolecular reaction
(b) second order reaction
(c) first order reaction
(d) unimolecular reaction

4. Which of the following is a monosaccharide?

(c) Lactose (d) Maltose
(c) Fructose (d) Cellulose

5. Solutions A, B, C and D are respectively 0.1 M glucose, 0.05 M NaCl, 0.05 M $BaCl_2$ and 0.1 M $AlCl_3$.
Which one of the following pairs is isotonic ?

(a) A and B (b) B and C
(c) A and D (d) A and C

6. Half-life of a reaction is found to be inversely proportional to the cube of initial concentration. The order of reaction is

(a) 4 (b) 3
(c) 5 (d) 2

Or

The rate of the reaction,

$$CCl_3CHO + NO \longrightarrow CHCl_3 + NO + CO$$

is equal to rate $k[CCl_3CHO]$ [NO]. If concentration is expressed in mol/L, the unit of k is

(a) $L\,mol^{-1}s^{-1}$ (b) $mol\,L^{-1}s^{-1}$
(c) $L^2mol^{-2}s^{-1}$ (d) s^{-1}

7. The pK_b values of different amines are given below.

S. No	Compound	pK_b
1.	Methanamine	3.38
2.	N,N-dimethyl aniline	8.92
3.	Ethanamine	3.29
4.	Phenyl methanamine	4.70

Among the given compounds, which one is the weakest base ?

(a) Methanamine
(b) N, N-dimethyl aniline
(c) Ethanamine
(d) Phenyl methanamine

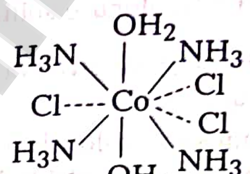
8. Iodoform test is not given by

(a) 2- pentanone (b) 3-pentanone
(c) ethanal (d) ethanol

9. Coordination number of Fe in $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ are respectively

(a) 2 and 3 (b) 6 and 6
(c) 6 and 3 (d) 6 and 4

Or

Give the name of 

(a) tetraammineaquacobalt chloride
(b) tetraamminediaquacobalt (III) chloride
(c) tetraamminediaquacobalt (IV) chloride
(d) None of the above

10. For the given rate expression= $k[A]^1[B]^1$, unit of rate constant is

(a) $mol^{-1}\,L\,s^{-1}$ (b) $mol^{-1}\,L\,s$
(c) $mol^{-1}\,L^{-1}$ (d) None of these

11. For the given rate expression = $k[A]^{3/2}[B]^{-1}$, the overall order of a reaction is

(a) zero (b) half
(c) one (d) two

Or

The unit of the rate constant of nth order is

(a) $mol^{1-n}\,L^{n-1}\,s^{-1}$
(b) $mol^{n-1}\,L^{1-n}\,s^{-1}$
(c) $mol^{n-1}\,L^{n-1}\,s$
(d) $mol^{n}\,L^{1-n}\,s^{-1}$

Assertion-Reason

In the following questions (Q.No. 12-16) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices.

(a) Both Assertion and Reason are correct statements and Reason is the correct explanation of the Assertion.
(b) Both Assertion and Reason are correct statements but Reason is not the correct explanation of the Assertion.
(c) Assertion is correct but Reason is incorrect statement.
(d) Assertion is incorrect but Reason is correct statement.

12. **Assertion** Glucose does not gives 2, 4-DNP test.
Reason Glucose exists in cyclic hemiacetal form.

13. **Assertion** Phenol is less acidic than *p*-nitrophenol.
Reason Phenolate ion is more stable than *p*-nitro phenolate ion.

14. **Assertion** Order of the following reaction,
$2NO(g)+2H_2(g) \longrightarrow 2H_2O(g)+N_2(g)$
is 3.
Reason Order of the reaction with respect to given reactant is the power of the reactant's concentration in the rate equation.

Or

Assertion Decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.
Reason At high pressure, the metal surface gets saturated with gas molecules.

15. **Assertion** In the coordination compound $[Co(H_2NCH_2CH_2NH_2)_3]_2$, ethane-1,2-diamine is a neutral molecule.
Reason Oxidation number of Co in the complex ion is +3.

16. **Assertion** Ethanol and acetone show positive deviation from Raoult's law.
Reason Pure ethanol molecule show hydrogen bond and on adding acetone hydrogen bond between ethanol molecules break.

SECTION B : *Short Answer Type I Questions*

17. Give the balanced equations for the following name reactions
(i) Rosenmund's reaction
(ii) Formaldehyde is treated with ammonia.

18. Name the type of isomerism shown by the following pair of compounds.
(i) $[CoCl(H_2O)(NH_3)_4]Cl_2$ and $[CoCl_2(NH_3)_4]Cl \cdot H_2O$
(ii) $[Pt(NH_3)_4][PtCl_6]$ and $[Pt(NH_3)_4Cl_2][PtCl_4]$

Or

Name the type of isomerism shown by the following pairs of coordination compounds.
(i) $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$
(ii) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ and $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

19. What are essential and non-essential amino acids? Give two examples each.

Or

Despite having an aldehyde group, glucose do not give 2, 4-DNP test. Why?

20. Answer the following questions :
(i) Give a chemical test to distinguish between methanol and dimethyl ether.
(ii) Which of the reagents between methanol and dimethyl ether will not react with Grignard reagent?

21. Deficiency of what vitamins cause following disease.
(i) Night blindness (ii) Scurvy

22. A 0.05 M NaOH solution offered a resistance of 31.6 Ω in a conductivity cell. If the cell constant of the conductivity cell is $0.378 \, cm^{-1}$, determine the molar conductance of NaOH solution at this temperature.

23. Complete the following chemical reaction equations:
(i) $MnO_4^-(aq) + C_2O_4^{2-}(aq) + H^+(aq) \longrightarrow$
(ii) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

24. For the given reaction,
$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
if $\Delta[NH_3]/\Delta t = 4 \times 10^{-8} \text{ mol L}^{-1}\text{s}^{-1}$, then what is the value of $-\Delta[H_2]/\Delta t$?

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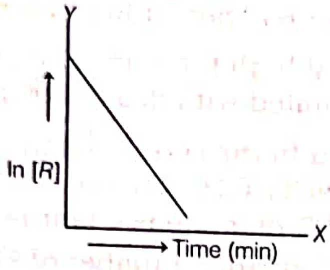
Or

Consider the following :
$\ln[R]$ vs time (min) plot.



(a) What is the order of the reaction?

(b) What are the units of rate constant, (k) for the reaction?

25. Write the structure of the major organic products in each of the following reactions :

(a) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

(b) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{Peroxide}}$

SECTION C : *Short Answer Type II Questions*

26. A strip of nickel metal is placed in a 1M solution of $Ni(NO_3)_2$ and a strip of silver metal is placed in a 1M solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter.

Given, $E^\circ_{Ni^{2+}/Ni} = -0.25$ V

$E^\circ_{Ag^+/Ag} = 0.80$ V

Write the balanced equations for the overall reactions occurring in the cell and calculate the cell potential.

27. $[CoF_6]^{3-}$ is a coordination complex ion

(i) What is the oxidation number of cobalt in the complex?

(ii) State the magnetic behaviour of the complex.

(iii) Give the IUPAC name of the complex.

Or

For the complex ion of $[Fe(CN)_6]^{3-}$

(i) Show hybridisation diagramatically.

(ii) Is it an inner orbital complex or an outer orbital complex?

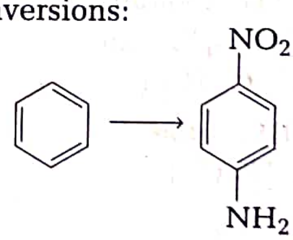
(iii) State its magnetic property.

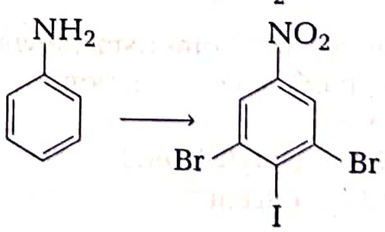
28. An organic compound '*A*' having molecular formula, C_6H_6O gives a characteristic colour with *aq*. $FeCl_3$ solution '*A*' on treatment with CO_2 and NaOH at 400 K under pressure gives '*B*', which on acidification gives a compound '*C*'. The compound '*C*' reacts with acetyl chloride to give '*D*' which is a popular pain killer. Deduce the structure of *A*, *B*, *C* and *D*.

29. Identify the compounds *A*, *B*, *C* and *D* required for the following conversion.

$$C_6H_5NO_2 \xrightarrow{[A]} C_6H_5NH_2 \xrightarrow{[B]} C_6H_5N_2^+Cl^- \xrightarrow{[C]} C_6H_5Cl \xrightarrow{[D]} C_6H_5OH$$

30. Write the steps to carry out the following conversions:

(i) 

(ii) 

Or

(i) Give reason for the following

(a) Gabriel phthalimide synthesis is not preferred for synthesising aromatic primary amines.

(b) *tert*-butylamine cannot be prepared by the action of NH_3 on *tert*-butyl bromide.

(ii) Give one chemical test to distinguish between ethyl nitrile and nitroethane.

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SECTION D : Long Answer Type Questions

31. (i) 100 mg of a protein is dissolved in enough water to make 10.0 mL of a solution. If this solution has an osmotic pressure of 13.3 mm Hg at 25°C, what is the molar mass of protein? ($R = 0.0821$ L atm mol^{-1} K^{-1} and 760 mm Hg = 1 atm)

(ii) What is the molarity of H_2SO_4 solution which has a density 1.84 g/cc at 35°C and contains 98% by weight ?

Or

(i) Define each of the following :

(a) Osmotic pressure

(b) Ebullioscopic constant

(ii) At some temperature, the vapour pressure of pure C_6H_6 is 0.256 bar and that of pure $C_6H_5CH_3$ (toluene) is 0.0925 bar. If the mole fraction of toluene is 0.0925 bar. If the mole fraction of toluene in solution is 0.6. Then,

(a) what will be the total pressure of the solution?

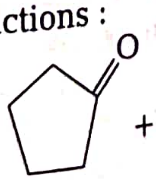
(b) what will be the mole fraction of each component in vapour phase ?

32. (i) An organic compound A with the molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative which reduces Tollen's reagent and undergoes Cannizzaro reaction.
On vigorous oxidation, it gives 1,2-benzene dicarboxylic acid.
Identify the compound A.

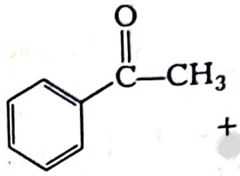
(ii) Give simple chemical tests to distinguish between the following pairs of compounds:
Ethanal and propanal.

Or

(i) Predict the products of the following reactions :

(a)  $+ NH_2{-}OH \xrightarrow{H^+}$

(b) $R{-}CH{=}CH{-}CHO + NH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}NH_2 \xrightarrow{H^+}$

(c)  $+ CH_3CH_2NH_2 \xrightarrow{H^+}$

(ii) Give the chemical reaction of the following :

(a) Bromination of phenol to 2, 4, 6-tribromophenol.

(b) Hydroboration of propene and then oxidation to propanol.

33. (i) Write down the electronic configuration of

(a) Cr^{3+} (b) Cu^+

(c) Co^{2+} (d) Mn^{2+}

(ii) Describe the cause of the following variations :

(a) Cr^{2+} is stronger reducing agent than Fe^{2+}.

(b) $E°(M^{2+}/M)$ value for copper is positive (+ 0.34 V).

(c) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents, it is easily oxidised.

Or

(i) Calculate the magnetic moment of a divalent ion in aqueous solution $[Fe(H_2O)_6]^{2+}$, if atomic number of Fe is 26.

(ii) Explain the following :

(a) Why does Cu not displace hydrogen from acids?

(b) Why $E°$ values for Mn, Ni and Zn are more negative than expected?

(c) Why first ionisation of Cr is lower than that of Zn ?

Solutions

1. (i) (c) Here, $\Lambda_m = \dfrac{\kappa \times 1000}{M}$

$$= \frac{7.896 \times 10^{-5} \times 1000}{0.00241}$$

$$\Lambda_m = 32.76 \quad (1)$$

(ii) (b) $\Lambda_m = \dfrac{1000 \times \kappa}{\text{Molarity}}$ or $\kappa = \dfrac{\Lambda_m \times \text{Molarity}}{1000}$

$$= \frac{1.26 \times 10^{-2} \times 0.01}{1000} = 1.26 \times 10^{-3} \quad (1)$$

(iii) (d) The increase in molar conductivity of any strong electrolyte like HCl with dilution is due to decrease in the interionic forces. (1)

Or

(a) $\Lambda_m = \kappa \times V$, where V is the volume of solution containing 1 mole of the solute. Specific conductivity (κ) decreases with dilution but volume increases much more on dilution. Hence, Λ_m increases with dilution. As volume containing 1 mole of NaCl will be highest for 0.005 M NaCl solution, the product of $\kappa \times V$ will be highest and hence Λ_m will also be highest. (1)

(iv) (d) Statement (d) is wrong about molar conductivity. Glucose is a non-electrolyte and hence question of having molar conductivity does not arise. (1)

2. (i) (b) Both Assertion and Reason are true but Reason is not the correct explanation of Assertion.

Greater the molecular mass, stronger the van der Waals' forces of attraction and hence higher is the melting point/boiling point. (1)

(ii) (c) Assertion is correct but Reason is incorrect.

Due to symmetrical nature and more close packing, *p*-dichlorobenzene has high melting point. (1)

(iii) (c) Assertion is correct but Reason is incorrect.

Alkyl iodides in general turn brown due to liberation of I_2 on their decomposition by the action of air and light. (1)

Or (c) Assertion is correct but Reason is not correct.

Even though haloalkanes are polar molecules, still they are insoluble in water. This is due to the fact that haloalkanes can neither form hydrogen bonds with water nor they can break the hydrogen bonds already existing between water molecules. (1)

(iv) (a) Both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

For a given halogen the boiling point rises with increasing atomic mass of the halogen, so that fluoride has the lowest boiling point and iodide has the highest boiling point. (1)

3. (b) A zero order reaction is a multistep reaction.

Or (d) In a reaction involving two different reactants can never be unimolecular reaction. (1)

4. (c) Fructose is a monosaccharide. It is a simple carbohydrate which are composed of single unit of saccharide and cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone. (1)

5. (a) Isotonic solutions have same molar concentration of solute particles in solution. Molar concentration of solute particles in solution are 0.1 M in glucose, 2×0.05 M in NaCl, 3×0.05 in $BaCl_2$ and 4×0.1 in $AlCl_3$. Therefore, 0.1 M glucose (*A*) and 0.05 M NaCl (*B*) solutions are isotonic. (1)

6. (a) $t_{1/2} \propto \dfrac{1}{a^{n-1}}$

when, $t_{1/2} \propto \dfrac{1}{a^3}$

$n - 1 = 3 \Rightarrow n = 3 + 1 = 4$

Hence, order of reaction = 4 (1)

Or

(a) Rate $= \dfrac{dx}{dt} = k[CH_3CHO][NO]$

$$k = \frac{dx}{dt \times [CCl_3CHO][NO]}$$

$$= \frac{\text{mol/L}}{\text{s} \times \text{mol/L} \times \text{mol/L}}$$

$$= \text{L mol}^{-1}\text{s}^{-1} \quad (1)$$

7. (b) Smaller the value of pK_b, stronger is the base. Since the value of pK_b for N, N-dimethyl aniline is the highest among the given compounds, it is the weakest base. (1)

8. (b) Since, 3-pentanone does not contain $\left(CH_3-\underset{\underset{O}{\|}}{C}-\right)$ group, it does not give iodoform test. (1)

9. (b) The number of ligands attached to the central metal ion is called the coordination number.

So, coordination number of Fe in $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ are 6 and 6 respectively. (1)

Or

(b) The IUPAC name of the given compound is tetraamminediaquacobalt (III) chloride. (1)

10. (a) Rate $= k[A]^1 [B]^1$

$$k = \frac{\text{Rate}}{[A][B]^1}$$

$$= \frac{\text{mol L}^{-1}\text{s}^{-1}}{[\text{mol L}^{-1}]^2} \Rightarrow \text{mol}^{-1}\text{L s}^{-1} \quad (1)$$

11. (a) Rate $= k[A]^x[B]^y$

Order $= x + y$

$\therefore$ Order is $\left(\frac{3}{2}\right) + (-1) = 1/2$, i.e. half-order. **(1)**

Or

(a) The units of rate constant of n^{th} order is $mol^{1-n}L^{n-1}s^{-1}$. **(1)**

12. (a) Both Assertion and Reason are true and Reason is the correct explanation of Assertion. **(1)**

13. (c) Phenol is less acidic than *p*-nitrophenol because $—NO_2$ is strongly electron withdrawing group *p*-nitrophenolate ion is more stable than phenolate ion. Hence, Assertion is correct but Reason is incorrect. **(1)**

14. (a) Order of the following reaction,
$2NO(g) + 2H_2(g) \longrightarrow 2H_2O(g) + N_2(g)$ is 3. As we know that, order of the reaction with respect to given reactant is the power of the reactants concentration in the rate equation.

Thus, both Assertion and Reason are correct and Reason is the correct explanation of Assertion. **(1)**

Or

(a) It is a zero order reaction at high pressure.

$$2NH_3(g) \xrightarrow[\text{Pt catalyst}]{1130\text{ K}} N_2(g) + 3H_2(g)$$

$$\text{Rate} = k\,[NH_3]^0 = k$$

In this reaction, Pt acts as a catalyst the metal surface gets saturated with gas molecules at high pressure.

Thus, a further change in reaction conditions does not alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration. **(1)**

15. (*b*) Ethane-1, 2-diamine is a neutral molecule as it carries no charge. Oxidation number of Co in the complex ion is +3.

Both Assertion and Reason are correct but Reason is not the correct explanation of Assertion. **(1)**

16. (a) Ethanol molecule shows hydrogen bonding. On adding acetone, its molecules get in between the host molecule and break some of hydrogen bonds between them. Due to weakening of interaction, the mixture of ethanol and acetone shows the positive deviation from Raoult's law.

Thus, Both Assertion and Reason are correct and Reason is the correct explanation of Assertion. **(1)**

17. (i) Rosenmund's reaction

$$CH_3-\overset{\overset{O}{||}}{C}-Cl + H_2 \xrightarrow[\text{Boiling xylene}]{Pd,\ BaSO_4} CH_3-\overset{\overset{O}{||}}{C}-H + HCl$$ **(1)**

(ii) When formaldehyde is treated with ammonia, then urotropine is formed.

$$6H-\overset{\overset{O}{||}}{C}-H + 4NH_3 \longrightarrow \underset{\text{Urotropine}}{(CH_2)_6N_4} + 6H_2O$$ **(1)**

18. (i) $[CoCl(H_2O)(NH_3)_4]Cl_2$ and $[CoCl_2(NH_3)_4]Cl \cdot H_2O$ the difference is in the number of water molecule present as ligand (i.e. in coordination sphere) and as molecule of water of crystallisation (i.e. outside the coordination sphere). Hence, they are called **hydrate isomers.** **(1)**

(ii) In these compounds, both positive and negative ions of salt are complex ions and the two isomers differ in the distribution of ligands in cation and anion. Hence, they are **coordination isomers**. **(1)**

Or

(i) In both compounds, ambident ligand NO_2 is present. In $[Co(NH_3)NO_2]Cl_2$, NO_2 is coordinated through N and in $[Co(NH_3)_5ONO]Cl_2$, NO_2 is coordinated through O. Hence, they show linkage isomerism. **(1)**

(ii) These isomers differ from each other in number of water molecules coordinated to central metal atom, i.e. (Cr). So, they show hydrate isomerism. **(1)**

19. Amino acids which are synthesised by the body are called non-essential amino acid, e.g. glycine, alanine. The amino acids which cannot be synthesised in the body and must be obtained from diet are known as essential amino acids. e.g. lysine, valine etc. **(2)**

Or

Although, glucose in its open chain structure contains a free aldehydic group yet, it does not give 2, 4-DNP test, a characteristic reaction of aldehydes, i.e. —CHO groups. This is because glucose actually exists in the cyclic hemiacetal form with only a small amount of the open chain form in equilibrium. Since, the concentration of the open chain form is very low and its reactions with 2, 4-DNP are reversible, thus its 2, 4-DNP adduct is generally not observed. **(2)**

20. (i) It can be distinguished by the reaction with Na as shown below :

$$2CH_3OH + 2Na \longrightarrow 2CH_3\overset{-}{O}\overset{+}{Na} + H_2\uparrow$$

$$CH_3OCH_3 + Na \longrightarrow \text{No change}$$

Methanol reacts with sodium to liberate hydrogen gas and dimethyl ether does not react with sodium. **(1)**

(ii) Dimethyl ether being aprotic is unreactive towards Grignard reagent. **(1)**

21. Deficiency of vitamin A causes night blindness and deficiency of vitamin C causes scurvy. **(2)**

22. Given, concentration $C = 0.05$ M,
resistance $(R) = 31.6\,\Omega$,
cell constant $(G) = 0.378\ cm^{-1}$,

Molar conductance,

$$\Lambda_m = \frac{1000}{0.05} \times \frac{0.378}{31.6}$$
$$= 239.24\,\Omega^{-1}\,cm^2\,mol^{-1}$$ (2)

23. (i) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$ (1)

(ii) $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$ (1)

24. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$$\text{Rate of reaction} = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

$$\therefore \quad -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

$$\frac{-\Delta[H_2]}{\Delta t} = \frac{3}{2} \times 4 \times 10^{-8}$$
$$= 6 \times 10^{-8}\,mol\,L^{-1}s^{-1}$$ (2)

Or

(a) The given plot shows the first order reaction.

(b) Unit of $k = (mol\,L^{-1})^{1-n}\,s^{-1}$
$$= (mol\,L^{-1})^{1-1}\,s^{-1} = s^{-1}$$ (2)

25. (a) $\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + SOCl_2 \xrightarrow{\text{Pyridine}} \underset{\text{1-chloropropane}}{CH_3CH_2CH_2Cl} + SO_2\uparrow + HCl$ (1)

(b) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2CH_2Br$ (1)

26. Half-cell reactions for the given case are as follows :

At anode (oxidation)

$Ni\,(s) \longrightarrow Ni^{2+}\,(1M) + 2e^-$; $E^\circ_{Ni^{2+}/Ni} = -0.25\,V$ (1/2)

At cathode (reduction)

$2Ag^+(1M) + 2e^- \longrightarrow 2Ag(s)$; $E^\circ_{Ag^+/Ag} = 0.80\,V$ (1/2)

Thus, the overall reaction is

$$Ni + 2Ag^+ \longrightarrow Ni^{2+} + 2Ag$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E^\circ_{Ag^+/Ag} - E^\circ_{Ni^{2+}/Ni}$$

$$\therefore \quad E^\circ_{cell} = 0.80 - (-0.25) = 1.05\,V$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[Ni^{2+}]}{[Ag^+]^2} \quad [\because n = 2]$$

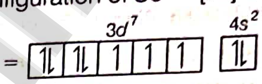
$$E_{cell} = 1.05 - \frac{0.059}{2}\log(1)$$
$$= 1.05 - \frac{0.059}{2} \times 0 = 1.05\,V$$ (2)

27. (i) Let the oxidation number of Co in the complex ion $[CoF_6]^{3-}$ is x, then

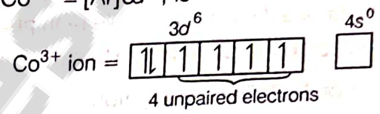
$x + 6(-1) = -3$

$\Rightarrow \quad x = +3$ (1)

(ii) Electronic configuration of Co = $[Ar]\,3d^7, 4s^2$



For $Co^{3+} = [Ar]3d^6, 4s^0$



Therefore, there are 4 unpaired electrons.

Thus, it is paramagnetic.

(iii) Hexaflouridocobalt (III) ion.

Or

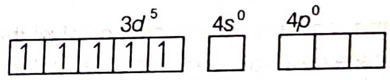
(i) Let the oxidation number of Fe in the complex ion $[Fe(CN)_6]^{3-}$ be x

Then, $x + 6(-1) = -3$

$\Rightarrow \quad x = +3$

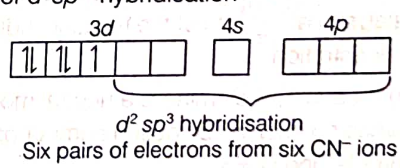
Electronic configuration

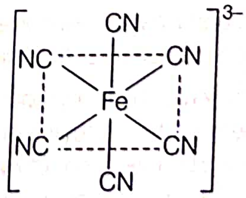
$\Rightarrow \quad Fe = [Ar]\,3d^6 4s^2$



CN^- being strong field ligand, paired up the d-electrons of the metal

For d^2sp^3 hybridisation





Structure octahedral

$[Fe(CN)_6]^{3-}$ (1)

(ii) It is an inner orbital complex as inner d-orbitals take part in hybridisation. (1)

(iii) It is paramagnetic due to the presence of unpaired electron. (1)

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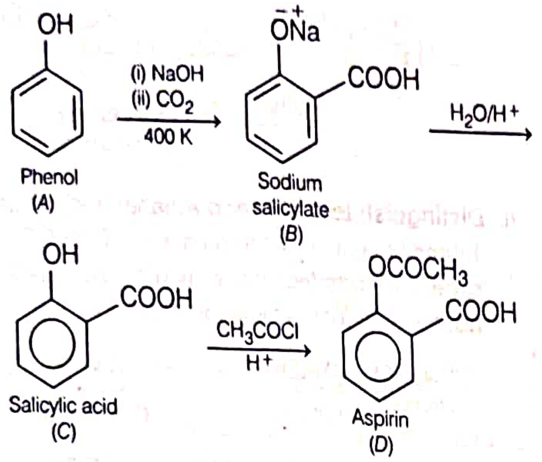
28.



(3)

29. $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow[\text{[A]}]{Sn+HCl} \underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[\text{[B]}]{NaNO_2+HCl} C_6H_5\overset{+}{N_2}\overset{-}{Cl}$

$C_6H_5\overset{+}{N_2}\overset{-}{Cl} \xrightarrow[\text{[C]}]{Cu_2Cl_2/HCl} \underset{\text{Chlorobenzene}}{C_6H_5Cl} \xrightarrow[\text{[D]}]{2NaOH+Dil.HCl} \underset{\text{Phenol}}{C_6H_5OH}$

(2)

$\therefore A \longrightarrow Sn + HCl$

$B \longrightarrow NaNO_2 + HCl$

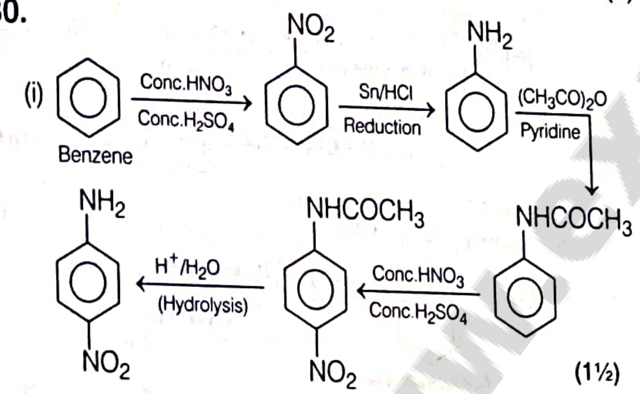
$C \longrightarrow Cu_2Cl_2/HCl$

$D \longrightarrow 2NaOH + Dil.HCl$

(1)

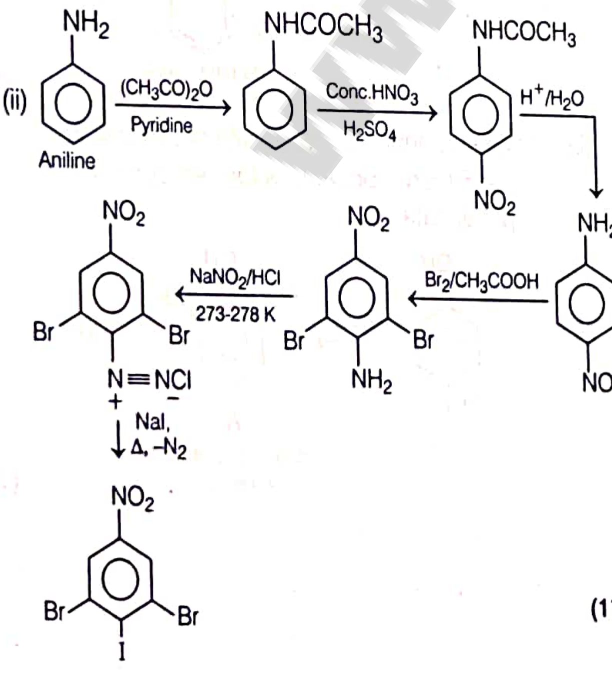
30.

(i)



(1½)

(ii)



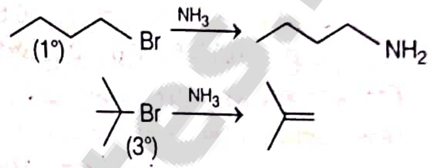
(1½)

Or

(i) (a) Gabriel phthalimide method is not useful for the preparation of aromatic primary amines because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide. **(1)**

(b) Ammonolysis (action of NH_3) gives the highest yield with 1° halides where substitution predominates because 1° halides behave as nucleophile while in case of 3° halide elimination predominates, where 3° halide acts as base.

Therefore, *tert*-butylamine cannot be prepared by the action of NH_3 on *tert*-butyl bromide.



(1)

(ii) **Ethyl nitrile** (C_2H_5CN) **and nitroethane** ($C_2H_5NO_2$).

Nitroethane gives a blood red colouration when treated first with nitrous acid and then with aqueous NaOH solution. Ethyl nitrile, however, does not give this test. The reactions are given below:

$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} \xrightarrow[\text{Aq. NaOH}]{HNO_2} \underset{\text{Nitrolic acid}}{CH_3-\underset{\underset{NOH}{\|}}{C}-NO_2} \xrightarrow{NaOH} \underset{\substack{\text{Sodium nitrolate}\\ \text{Blood red colouration}}}{CH_3-\underset{\underset{NO\overset{-}{}\overset{+}{Na}}{\|}}{C}-NO_2}$$

(1)

31. (i) Mass of protein, $w = 100 \text{ mg} = 0.1 \text{ g}$

Volume of solution, $V = 10 \text{ mL} = 0.01 \text{ L}$

Osmotic pressure, $\pi = 13.3 \text{ mm Hg} = \frac{13.3}{760} \text{ atm}$

$= 0.0175 \text{ atm}$

$R = 0.0821 \text{ L atm mol}^{-1} \text{K}^{-1}$

$T = 25°C = (25 + 273) \text{ K} = 298 \text{ K}$

Using the formula,

Molar mass of protein, $M = \frac{wRT}{\pi V}$

$$= \frac{0.1 \text{ g} \times 0.0821 \text{ L atm mol}^{-1} \text{K}^{-1} \times 298 \text{ K}}{0.0175 \text{ atm} \times 0.01 \text{ L}}$$

$= \mathbf{13980.5 \text{ g mol}^{-1}}$ **(3)**

(ii) Molarity $(M) = \frac{\text{Mass of solute} \times 1000}{\text{Molecular mass} \times \text{volume}}$

$V = \frac{M}{D} = \frac{100}{1.84}$

$M = \frac{98 \times 1000 \times 1.84}{98 \times 100} = 18.4 \text{ M}$

(2)

Or

(i) (a) The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis, i.e. to stop the passage of solvent molecules through a semipermeable membrane into the solution.

It is a colligative property as it depends upon the number of solute molecules and not on their nature. (1)

(b) It is defined as the elevation in boiling point for 1 molal solution. It is denoted as K_b. (1)

(ii) (a) According to Raoult's law,

For toluene, $p_1 = p_1^\circ \times \chi_1$

$p_1^\circ = 0.0925$ bar and $\chi_1 = 0.6$

Then, $p_1 = 0.0925 \times 0.6 = 0.0555$ bar (1/2)

For benzene, $p_2 = p_2^\circ \times \chi_2$

Mole fraction of benzene,

$\chi_2 = 1 - \chi_1 = 1 - 0.6 = 0.4$

and $p_2^\circ = 0.256$ bar

Then, $p_2 = 0.256 \times 0.4 = 0.1024$ bar (1/2)

Total vapour pressure of solution,

$p_{total} = p_1 + p_2$

$= 0.0555 + 0.1024 = 0.158$ bar (1)

(b) Mole fraction of toluene in vapour phase,

$$y_1 = \frac{p_1}{p_{total}} = \frac{0.0555}{0.158} = 0.351$$ (1/2)

Mole fraction of benzene in vapour phase,

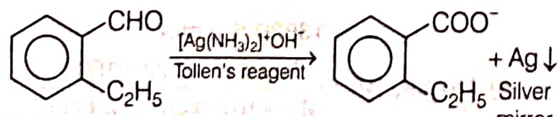
$$y_2 = \frac{p_2}{p_{total}} = \frac{0.1024}{0.158} = 0.648$$ (1/2)

32. (i) (a) As the given compound with molecular formula $C_9H_{10}O$ forms a 2,4-DNP derivative and reduces Tollen's reagent, thus it must be an aldehyde. (1/2)

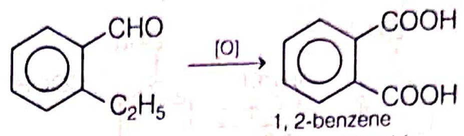
(b) As it undergoes Cannizzaro reaction, hence —CHO group is directly attached to the benzene ring. (1/2)

(c) On vigorous oxidation, it gives 1,2-benzene dicarboxylic acid. Therefore, it must be an *ortho*-substituted benzaldehyde and the only *o*-substituted aromatic aldehyde which have $C_9H_{10}O$ molecular formula is *o*-ethyl benzaldehyde. (1)

Reactions involved



o-ethyl benzaldehyde 2-ethylbenzoate



1, 2-benzene dicarboxylic acid (1)

(ii) **Distinguish test between ethanal and propanal**

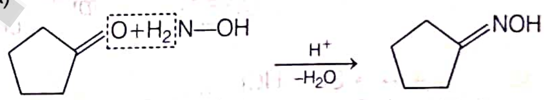
Ethanal because of the presence of CH_3CO skeleton gives iodoform test, whereas propanal due to the absence of such a skeleton does not. (1)

$$\underset{\text{Ethanal}}{CH_3CHO} + \underset{\text{Sodium hydroxide}}{4NaOH} + 3I_2 \longrightarrow \underset{\substack{\text{Iodoform}\\\text{(yellow ppt.)}}}{CHI_3\downarrow} + HCO\overset{-}{O}\overset{+}{N}a + \underset{\text{Sodium iodide}}{3NaI} + 3H_2O$$

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{Sodium hydroxide}}{4NaOH} + 3I_2 \longrightarrow \text{No reaction}$$ (1)

Or

(i) (a)

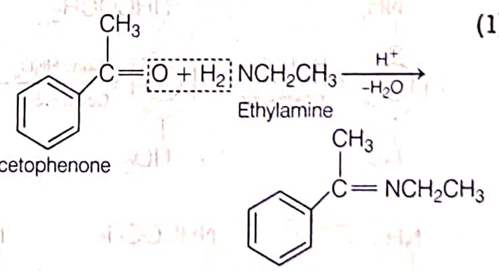


Cyclopentanone Hydroxylamine Cyclopentanone oxime (1)

(b) $$\underset{\text{Unsaturated aldehyde}}{R\text{—}CH{=}CH\text{—}CH\boxed{O + H_2}}\underset{\text{Semicarbazide}}{N\text{—}NH\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NH_2} \xrightarrow[-H_2O]{H^+}$$

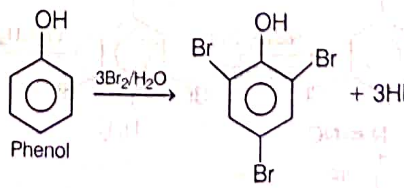
$$\underset{\text{Semicarbazone}}{R\text{—}CH{=}CH\text{—}CH{=}N\text{—}NH\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NH_2}$$ (1)

(c)



Acetophenone Ethylamine Schiff's base (1)

(ii) (a) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



Phenol 2, 4, 6-tribromophenol (white ppt.) (1)

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(b)
$$CH_3—CH{=}CH_2 + (H—BH_2)_2 \xrightarrow{\text{(Anti-Markownikoff's Addition)}}$$
Propene

$$\underset{\substack{| \\ H}}{CH_3—CH}—\underset{\substack{| \\ BH_2}}{CH_2} \xrightarrow{CH_3—CH{=}CH_2}$$

$$(CH_3—CH_2—CH_2)_2B \xrightarrow[3H_2O_2,\ \bar{O}H]{H_2O}$$

$$B(OH)_3 + 3CH_3—CH_2—CH_2—OH$$
Propan-1-ol

(1)

33. (i) (a) $Cr^{3+} (Z = 24) = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

Here, $1s^2 2s^2 2p^6 3s^2 3p^6$ refer to the electronic configuration of $[Ar]^{18}$, thus electronic configuration of Cr^{3+} can be written as:

$Cr^{3+} = [Ar]\,3d^3$

(b) $Cu^+ (Z = 29) = [Ar]^{18} 3d^{10}$

(c) $Co^{2+} (Z = 27) = [Ar]^{18} 3d^7$

(d) $Mn^{2+} (Z = 25) = [Ar]^{18} 3d^5$ (2)

(ii) (a) In case of,

$Cr^{2+} \longrightarrow Cr^{3+}, E°(Cr^{3+} \longrightarrow Cr^{2+}) = -0.26\,V$

$Cr^{2+} \longrightarrow Cr^{3+}, E° = 0.26\,V$

In case of,

$Fe^{2+} \longrightarrow Fe^{3+}, E°(Fe^{3+}) \longrightarrow Fe^{2+} = +0.77\,V$

$Fe^{2+} \longrightarrow Fe^{3+}, E° = -0.774\,V$

Thus, the order of strength for Cr^{2+} and Fe^{2+} as reducing agents is $Cr^{2+} > Fe^{2+}$. (1)

(b) High sublimation and ionisation enthalpies and low enthalpy of hydration are responsible for possible $E°\,Cu^{2+}/Cu^+$. (1)

(c) Cobalt (III) ion has greater tendency to form complexes than cobalt (II) ion.

Therefore, Co (II) ion being stable in aqueous solution, changes to Co (III) ion in the presence of complexing reagents and gets oxidised. (1)

Or

(i) Magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM

Atomic number of Fe = 26 = $[Ar]\,3d^6 4s^2$

$Fe^{2+} = [Ar]\,3d^6 4s^0 = \boxed{1\!\downharpoonright}\boxed{1}\boxed{1}\boxed{1}\boxed{1}$

So, $\mu = \sqrt{n(n+2)}$

$= \sqrt{4(4+2)} = \sqrt{24} = 4.89\,BM$ (2)

(ii) (a) Since, Cu lies below hydrogen in electro-chemical series and has a positive value of electrode potential, it cannot displace hydrogen from acids.

(b) Mn^{2+} and Zn^{2+} have stable half-filled and fully-filled electronic configuration respectively. Ni has highest negative enthalpy of hydration. Therefore, the $E°$ values for Mn, Ni and Zn are more negative than expected.

(c) The electronic configuration of Cr and Zn are

$Cr = [Ar]3d^5 4s^1$

$Zn = [Ar]\,3d^{10} 4s^2$

By losing an electron, Cr attains stable d^5 configuration. In Zn, electron has to be removed from 4s-orbital which is held more strongly by the nucleus. Therefore, the first ionisation enthalpy of Cr is lower than that of Zn. (3)

SAMPLE QUESTION PAPER 3

A HIGHLY SIMULATED SAMPLE QUESTION PAPER FOR CBSE CLASS XII

CHEMISTRY [Unsolved]

Instructions

1. There are 33 questions in this question paper. All questions are compulsory.
2. **Section A :** Q. No. 1 to 16 are Objective Type Questions. Q. No. 1 and 2 are Case Based Questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
3. **Section B :** Q. No. 17 to 25 are Short answer type I questions and carry 2 marks each.
4. **Section C :** Q. No. 26 to 30 are Short answer type II questions and carry 3 marks each.
5. **Section D :** Q. No. 31 to 33 are Long answer questions carrying 5 marks each.
6. There is no overall choice. However, an internal choices have been provided.
7. Use of calculators and log tables is not permitted.

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SECTION A : *Objective Questions*

Case Based Questions

1. *Read the passage given below and answer the following questions :* (1×4=4)

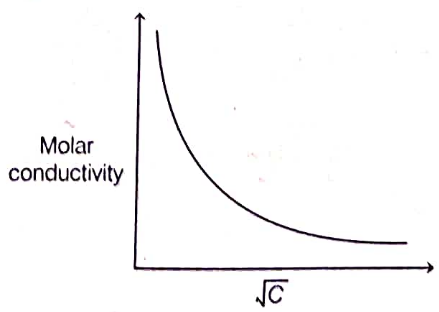
The magnitude of conduction depends upon the nature of the material. It also depends upon the temperature and pressure at which the measurements are made. Materials are classified into conductors, insulation and semiconductors. It depends on the magnitude of their conductivity.

Electrical conductance through metal is due to the movement of electrons and termed as electronic or metallic conductance. It depends upon the nature and structure of metal, number of valence electrons per atom and temperature (it decreases with increase of temperature).

Pure water has very low conductivity but when electrolytes are dissolved in water, they furnish their own ions in the solution, hence its conductivity increases. The conductance of electricity by ions which are present in the solutions is called electrolytic or ionic conductance. The conductivity of electrolytic solutions depends on the nature of the electrolyte, size of the ions produced and their solution, nature of the solvent and its viscosity, concentration of the electrolyte and temperature (it increases with the increase in temperature).

(i) The conductivity of strong electrolyte
   (a) increases on dilution slightly
   (b) decreases on dilution
   (c) does not change with dilution
   (d) depends upon density of electrolyte itself

(ii) The variation of molar conductivity with concentration of an electrolyte (X) in aqueous solution is shown in given figure.



The electrolyte X is

(a) HCl (b) NaCl

(c) KNO_3 (d) CH_3COOH

(iii) SI unit of molar conductivity is

(a) Sm^2mol^{-1} (b) $S^2m^2mol^{-1}$

(c) Sm^2mol^{-2} (d) $S^2m^2mol^{-2}$

(iv) The specific conductance of 0.1 N KCl solution at 23°C is 0.012 $ohm^{-1}cm^{-1}$. The resistance of cell containing the solution at the same temperature was found to be 55 ohm. The cell constant will be

(a) $0.66\,cm^{-1}$ (b) $1.12\,cm^{-1}$

(c) $0.918\,cm^{-1}$ (d) $1.66\,cm^{-1}$

Or

The conductivity of 0.01 N solution is found to be 0.005 $ohm^{-1}cm^{-1}$. The equivalent conductivity of the solution will be

(a) $5\times10^{-2}\ ohm^{-1}cm^2eq^{-1}$

(b) $5.00\times10^{-3}\ ohm^{-1}cm^2$

(c) $500\,ohm^{-1}cm^2eq^{-1}$

(d) $0.5\,ohm^{-1}cm^2equi^{-1}$

Answer

(i) (a) (ii) (d) (iii) (a) (iv) (a) or (c)

2. *Read the passage given below and answer the following questions :* (1×4=4)

The spontaneous flow of solvent molecules from solvent side to solution side or from a region of lower concentration to a region of higher concentration through a semipermeable membrane is called osmosis. It is different from that of diffusion, where the movement is in reverse direction. The minimum pressure that has to be exerted/applied on the solution to prevent the entry of solvent into solution through semipermeable membrane is called osmotic pressure.

This concept is used in desalination of sea water. The growth of plants depends mainly on the phenomenon of osmosis. Two solutions having same osmotic pressure are called **isotonic.**

Osmotic pressure is a colligative property. Molecular mass of a solute can be determined from the osmotic pressure measurements. Osmotic pressure is represented by π. Also, $\pi V = nRT$.

When there are two solutions and if one of the solutions is of lower osmotic pressure, it s called **hypotonic** and the other is called **hypertonic** with respect to other the osmotic pressure can be experimentally measured by using Berkeley Heartley method.

In these questions (i-iv) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices :

(a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.

(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.

(c) Assertion is correct statement but Reason is incorrect statement.

(d) Assertion is incorrect statement but Reason is correct statement.

(i) **Assertion** Osmosis is one sided movement solvent molecules.

Reason In osmosis the net movement of solvent particles from lower concentration towards higher concentration takes place through semipermeable membrane.

(ii) **Assertion** For isotonic solution, $C_1 = C_2$.

Reason For isotonic solution, $\pi_1 = \pi_2$.

(iii) **Assertion** Osmotic pressure of non-aqueous solutions can be determined by Berkeley Heartley method.

Reason The semipermeable membrane used in Berkeley Hartley method is $Cu_2[Fe(CN)_6]$.

(iv) **Assertion** If red blood cells are removed from the body and placed in pure water pressure inside the cell increases.

Reason The concentration of salt content in the cell increases.

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Or **Assertion** Out of various colligative properties, osmotic pressure is used for determination of molecular masses of polymers.

Reason Polymers solutions do not posses a constant boiling point or freezing point.

Answers

(i) (d) (ii) (d) (ii) (d) (iv) (c) or (c)

Multiple Choice Questions

Following questions (No. 3-11) are multiple choice questions carrying 1 mark each.

3. According to IUPAC nomenclature, sodium nitroprusside is named as
   (a) sodium pentacyanonitrosyl ferrate (II)
   (b) sodium pentacyanonitrosyl ferrate (III)
   (c) sodium nitroferricyanide
   (d) sodium nitroferrocyanide

4. The cell constant of a conductivity cell
   (a) changes with change of electrolyte
   (b) changes with change of concentration of electrolyte
   (c) changes with temperature of electrolyte
   (d) remains constant for a cell

5. What is the magnetic moment of $K_3[FeF_6]$?
   (a) 3.87 BM (b) 4.89 BM
   (c) 5.91 BM (d) 6.92 BM

   Or

   The complex ion which has no *d*-electrons in the central atom is
   (a) $[MnO_4]^-$ (b) $[Co(NH_3)_6]^{3+}$
   (c) $[Fe(CN)_6]^{3-}$ (d) $[Cr(H_2O)_6]^{3+}$

6. When a solution of formaldehyde and KOH is heated, it will give
   (a) acetylene and methane
   (b) methanol and potassium formate
   (c) methanol and methane
   (d) methanol and acetylene

7. Which amino acid has phenolic —OH group as it backbone?
   (a) Glycine (b) Leucine
   (c) Serine (d) Tyrosine

8. The method used to separate primary, secondary and tertiary amines is
   (a) Hofmann method
   (b) Lucas method
   (c) Victor Meyer method
   (d) Kolbe method

   Or

   Basicity order of amines in aqueous solution.
   (a) $3° > 1° > 2° > NH_3$ (b) $3° > 2° > 1° > NH_3$
   (c) $2° > 1° > 3° > NH_3$ (d) $2 < 1° < 3° < NH_3$

9. Which one of the following gases has the lowest value of Henry's law constant?
   (a) N_2 (b) He (c) CO_2 (d) O_2

10. Replacement of Cl from chlorobenzene to give phenol requires drastic conditions but chlorine of 2, 4-dinitrochlorobenzene is readily replaced because
    (a) NO_2 makes ring electron rich at *ortho* and *para* position
    (b) NO_2 withdraws electrons from *meta* position
    (c) NO_2 donates electron to *meta* position
    (d) NO_2 withdraws electrons from *ortho* and *para* positions

    Or

    Chlorobenzene is
    (a) less reactive than benzyl chloride
    (b) more reactive than ethyl bromide
    (c) nearly same reactive as that of methyl chloride
    (d) more reactive than isopropyl chloride

11. Wet ether is not used as a solvent in Wurtz reaction, because the water present in it
    (a) hydrolysis *RX* to *R*OH
    (b) reduces *RX* to *RH*
    (c) destroy the Na-metal
    (d) reacts with *R*—*R*

    Or

    In the following reaction, identify X.
    Methyl magnesium bromide $+ X \longrightarrow$ 2-methyl
    (a) propanol (b) ethanone
    (c) propanone (d) butane

Answers

3. (b) 4. (d) 5. (c) or (a) 6. (b) 7. (d) 8. (a) or (a) 9. (c) 10. (d) or (a) 11. (c) or (c)

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Assertion-Reason

In the following questions (Q.No. 12-16) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices.

(a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.
(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.
(c) Assertion is correct statement but Reason is incorrect statement.
(d) Assertion is incorrect statement but Reason is correct statement.

12. Assertion Glucose and fructose are reducing sugars.

Reason Glucose and fructose contain a free aldehydic and ketonic group adjacent to a >CHOH group respectively.

13. Assertion Addition of HCN to carbonyl compounds gives cyanohydrins.

Reason Pure HCN reacts with aldehydes and ketones.

14. Assertion 2-chloro-3-methylbutane on treatment with alcoholic potash gives 2-methyl but-2-ene as major product.

Reason Above reaction occurs according to Saytzeff rule.

15. Assertion Alcohol and phenol can be distinguished by sodium hydroxide.

Reason Alcohol is more acidic than phenol.

16. Assertion The reaction,

$$H_2 + Br_2 \longrightarrow 2HBr$$

has molecularity of two.

Reason Order of the given reaction is 2.

Or **Assertion** In the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$ the rate of reaction is different in terms of N_2, H_2 and NH_3.

Reason Rate of reaction is equal to the rate of disappearance of formation divided by the stoichiometric coefficient.

Answers

12. (a) **13.** (c) **14.** (a) **15.** (c) **16.** (c) or (d)

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SECTION B : *Short Answer Type I Questions*

17. Arrange the following compounds in the increasing order of dipole moment. Give reason.

$CH_3CH_2CH_3, CH_3CH_2NH_2, CH_3CH_2OH$

18. Give one test to distinguish between glucose and fructose with relevant equation.

19. Calculate the emf for the given cell at 25°C

$Cr|Cr^{3+}(0.1\,M)||Fe^{2+}(0.01\,M)|Fe$

[Given, $E^\circ_{Cr^{3+}/Cr} = -0.74$ V

$E^\circ_{Fe^{2+}/Fe} = -0.44$ V]

[Ans. $E_{cell} = 0.261$ V]

20. What will be the correct order for the wavelength of absorption in the visible region for the following?

$[Ni(NO_2)_6]^{4-}, [Ni(NH_3)_6]^{2+}, [Ni(H_2O)_6]^{2+}$

Or

A coordination compound $CoCl_3 \cdot 4H_2O$ precipitates silver chloride, when treated with silver nitrate. This compound dissociates into two ions in solution. Write the structural formula of the compound and name it.

21. Give reason for the following :

(i) Physisorption decreases with increase of temperature.
(ii) Ester hydrolysis slow in the beginning and becomes fast after sometime.

22. Write the equations involved in the Williamson's ether synthesis of tertiary butyl methyl ether.

Or

Why is the reactivity of all the three classes of alcohols with conc. HCl and $ZnCl_2$ (Lucas reagent) different?

23. What happens, when NH_4OH solution is added dropwise to copper sulphate solution till excess?

Or $KMnO_4$ is a strong oxidising agent in acidic medium. To provide acidic medium H_2SO_4 is used instead of HCl. Why?

24. (i) The value of $\Lambda°$ for HCl, KCl and CH_3COOK are 425.1, 121.3 and $94.0\,\Omega^{-1}cm^2mol^{-1}$ respectively. Calculate $\Lambda°$ for acetic acid (CH_3COOH).
[**Ans.** $\Lambda° = 397.85\ cm^2\ mol^{-1}$]

(ii) How many coulombs of charge are required for the reduction of 1 mole of Cu^{2+} to Cu?
[**Ans.** 193000 C]

25. Name the two component of starch. How do they differ from each other structurally?

SECTION C : *Short Answer Type II Questions*

26. Give the structure of various amines with molecular formula C_3H_9N. State whether they are primary, secondary or tertiary amines?

27. (i) Write the systematic names of the following :

(a) $[Co(NH_3)_6]\,Cl_3$

(b) $[Pt(NH_3)_2Cl\,(NH_2CH_3)]\,Cl$

(ii) Write the formula of the following compounds:

(a) Sodium hexanitrito-N-cobaltate (III)

(b) Tetraaquadichlorochromium (III) chloride

(iii) Calculate the oxidation state of Cu in $[Cu(NH_3)_4]\,SO_4$.

Or Explain, why $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

28. (i) What is glycogen ? How is it different from starch?

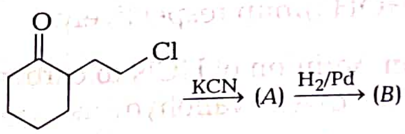
(ii) Which one of following is a disaccharide? Starch, Maltose, Fructose, Glucose

29. (i) Explain what happens when ethanol is heated with acetic acid in presence of conc. H_2SO_4?

(ii) Give one example of Clemmensen's reduction reaction.

Or

(i) Write the structure of A and B in the following reaction.

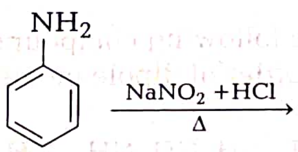


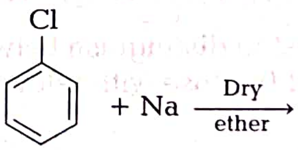
(ii) Convert the following :

(a) Nitrobenzene to benzoic acid

(b) Aniline to benzyl alcohol

30. (i) Complete the following reactions:

(a)


(b)


(ii) How is chlorobenzene halogenate in presence of halogen carrier? Write related equation.

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SECTION D : *Long Answer Type Questions*

31. (i) How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.

(ii) Give reason for the following :

(a) It is difficult to separate Zr and Hf.

(b) Fe^{3+} is more stable than Fe^{2+}.

Or (i) To what extent do the electronic configuration decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.

(ii) Explain the following trends in the properties of the members of 3*d*-series.

(a) Cu^{+} ion is not stable in aqueous solution.

(b) Mn exhibit maximum number of oxidation states.

32. For the reaction,

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

The following data were collected at 270 K.

Exp. No.	Initial [NO] mol L^{-1}	Initial [Cl_2] mol L^{-1}	Initial rate of disappearance of Cl_2 (mol/min)
1.	0.15	0.15	0.60
2.	0.15	0.30	1.20
3.	0.30	0.15	2.40
4.	0.25	0.25	*x*

(i) Write expression for rate law.

(ii) Calculate rate constant and write its unit.

[**Ans.** $K = 177.77\ mol^{-2}\ L^2\ min^{-1}$]

(iii) Find initial rate of disappearance of Cl_2 in experiment number (4).

[**Ans.** $r = 2.78$ mol/min]

Or

(i) Mention the factors that affect the rate of a chemical reaction.

(ii) A reaction is of second order with respect to a reactant. How is the rate of reaction affected, if the concentration of the reactant is

(a) doubled?

(b) reduced to half?

(iii) What is the effect of temperature on the rate constant of a reaction?

33. (i) How will you convert the following :

(a) Acetophenone to benzoic acid.

(b) Ethyl cyanide to ethanoic acid.

(c) Benzoic acid to benzaldehyde.

(ii) Write the structures of *A* and *B* are the following.

(a) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[\text{(ii)}\,H_2O]{\text{(i)}\,CH_3MgBr} A$

$\xrightarrow[\text{Ether}]{\text{Na-metal}} B$

(b) $CH_3CH_2Br \xrightarrow{NaOH\,(aq)} A \xrightarrow{PCC} B$

Or

A ketone $A\,(CH_2H_8O)$ which undergoes a haloform reaction gives compound *B* on reduction, heating with sulphuric acid gives a compound *C* which forms mono-ozonide *D*. *D* on hydrolysis with zinc dust gives only *E*.

Identify *A*, *B*, *C*, *D* and *E* write the reactions involved.

How does compound *A* gives iodoform reaction?

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SAMPLE QUESTION PAPER 4

A HIGHLY SIMULATED SAMPLE QUESTION PAPER FOR CBSE CLASS XII

CHEMISTRY [Unsolved]

Instructions

1. There are 33 questions in this question paper. All questions are compulsory.
2. **Section A :** Q. No. 1 to 16 are Objective Type Questions. Q. No. 1 and 2 are Case Based Questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
3. **Section B :** Q. No. 17 to 25 are Short answer type I questions and carry 2 marks each.
4. **Section C :** Q. No. 26 to 30 are Short answer type II questions and carry 3 marks each.
5. **Section D :** Q. No. 31 to 33 are Long answer questions carrying 5 marks each.
6. There is no overall choice. However, an internal choices have been provided.
7. Use of calculators and log tables is not permitted.

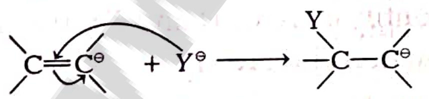
SECTION A : *Objective Questions*

Case Based Questions

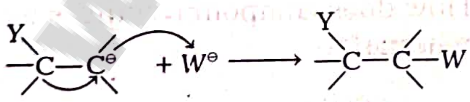
1. *Read the passage given below and answer the following questions :* (1×4=4)

Nucleophilic addition reactions are encountered in compounds containing polar functional groups (C=O, C≡N, C=S). In the first step, a nucleophile with its pair of electrons attacks the carbon atom of a double or triple bond, forming a carbanion. It is followed by a second step in which this carbanion reacts with a positive species.

Step I



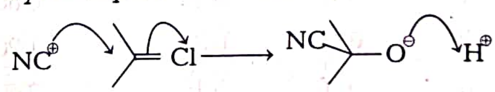
Step II



When the olefin contains a good leaving group (as defined for nuclepohilic substitution), substitution is a side reaction, (i.e. a nucleophilic substitution at a vinylic substrate).

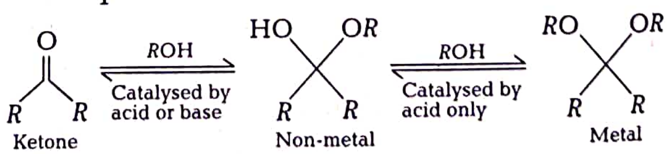
Addition of HCN to carbonyl group and addition of alcohol to carbonyl group is a nucleophilic addition reaction.

Addition of HCN to carbonyl group In this reaction cyanide ion (CN^-) acts as a nucleophile, which attacks the carbon of carbonyl group, the carbon-oxygen double bond breaks followed by capture of proton and a cyanohydrins is formed .



Addition of alcohol to carbonyl compounds Aldehydes are ketone react with one mole of alcohol to form hemiacetal or hemiketal, respectively. Reaction with second mole of alcohol gives acetal or ketal.

In this reaction the alcohol with lone pair of electrons of oxygen atom acts a sa nucleophile.



The following questions (i-iv) are multiple choice questions. Choose the most appropriate answer :

(i) Identify the example in which both nucleophilic addition and nucleophilic

addition elimination reaction occur, respectively in the carbonyl compound.

(a) Reduction to alcohols

(b) Addition of sodium sulphide

(c) Tollen's test

(d) Reaction with alcohols

(ii) Arrange the following carbonyl compounds in increasing order of their reactivity in nucleophilic addition reaction.

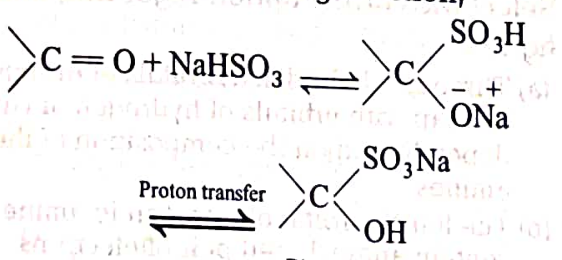
(a) Butanone < propanone < propanal < ethanal

(b) Butanone < propanal < propanone < ethanal

(c) Butanone < ethanal < propanone < propanal

(d) Butanone < ethanal < propanal < propanone

(iii) Consider the following reaction,



Bisulphite addition compound (crystalline)

In the given reaction, equilibrium lies largely to the right hand side for most aldehydes and the left for most ketones due to

(a) electronic reasons (b) steric reasons

(c) bonding reasons (d) Both (a) and (b)

(iv) Which of the following alternative is correct for the treatment of ketones with ethylene glycol in the presence of dry HCl?

(a) The product obtained is ethylene glycol hemi-ketal

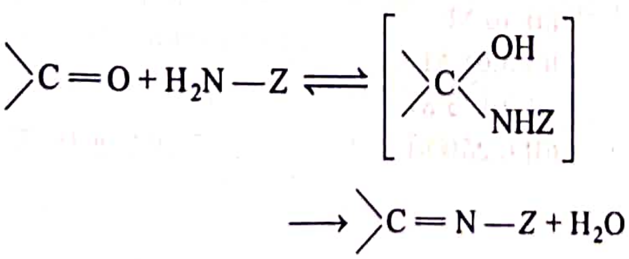
(b) In this reaction, electrophilicity of carbonyl carbon decreases

(c) HCl protonates the oxygen of the carbonyl group

(d) The product thus obtained is cyanohydrin

Or

Consider the following reaction,



Which of the following statement(s) is/are true about the above reaction?

(a) $H_2N—Z$ tends to add to the carbon of carbonyl group of aldehydes and ketones

(b) The reaction is reversible and catalysed by acid

(c) The equilibrium favours the product formation due to rapid dehydration of the intermediate

(d) All of the above

Answers

(i) (d) (ii) (a) (iii) (b) (iv) (c) or (d)

2. *Read the passage given below and answer the following questions :* (1×4=4)

Addition of a non-volatile solute to a solvent lowers its vapour pressure. Therefore, the vapour pressure of a solution (i.e. vapour pressure of solvent in a solution) is lower than that of pure solvent, at the same temperature. A higher temperature is needed to raise the vapour pressure upto one atmosphere pressure, when boiling point is attiained. However, increase in boiling point is small. For example, 0.1 molal aqueous sucrose solution boils at 100.05°C.

Sea water, an aqueous solution, which is rich in Na^+ and Cl^- ions, freezes about 1°C lower than frozed water. At the freezing point of a pure solvent, the rates at which two molecules stick together to form the solid and leave it to return to liquid state are equal when solute is present. Few solvent molecules are in contact with surface of solid. However, the rate at which the solvent molecules leave the surface of solid remains unchanged. That is why, temperature is lowered to restore the equilibrium. The freezing point depression in a dilute solution is proportional to molality of the solute.

In these questions (Q.No. i-iv) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices :

(a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.

(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.

(c) Assertion is correct statement but Reason is incorrect statement.
(d) Assertion is incorrect statement but Reason is correct statement.

(i) **Assertion** The molecular weight of acetic acid determined by depression in freezing point method in benzene and water was found to be different.
Reason Water is polar and benzene is non-polar.

(ii) **Assertion** When non-volatile solute is added to solvent, the vapour pressure of the solution decreases.
Reason As number of solvent molecules escaping from the surface is reduced, the vapour pressure of the solution is also reduced.

(iii) **Assertion** Freezing point of solvent is more than that of solution.
Reason When non-volatile solid is added to the solvent, its vapour pressure increases and become equal to solid solvent at the lower temperature.

(iv) **Assertion** The vapour pressure of a liquid decreases if some non-volatile solute is dissolved in it.
Reason The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution.

Or

Assertion The water pouch of instant cold pack for treating athletic injuries breaks, when squeezed and NH_4NO_3 dissolved lowering the temperature.
Reason Addition of non-volatile solute into solvent results into depression of freezing point of the solvent.

Answers

(i) (a) (ii) (a) (iii) (c) (iv) (b) or (a)

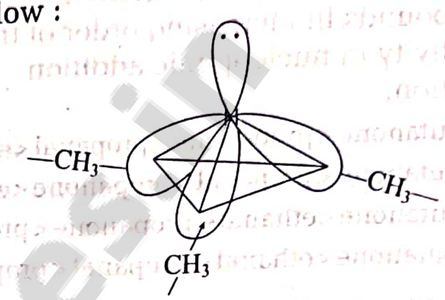
Multiple Choice Questions

Following questions (No. 3-11) are multiple choice questions carrying 1 mark each :

3. Which of the following aqueous solutions should have the highest boiling point ?
(a) 1.0 M NaOH (b) 1.0 M Na_2SO_4
(c) 1.0 M NH_4NO_3 (d) 1.0 M KNO_3

4. The rate constant 'k' for pseudo first order reaction is
(a) $\frac{2.303}{t}\log C_0 - C$ (b) $\frac{2.303}{t}\log \frac{C}{C_0}$
(c) $\frac{2.303}{t}\log C_0 + C$ (d) $\frac{2.303}{t}\log \frac{C_0}{C}$

5. The figure of trimethylamine is given below :



Select the correct option regarding above figure.
(a) Three sp^3-hybridised orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending upon the composition of the amines
(b) The fourth orbital of nitrogen in amines contain an unshared pair of electrons
(c) Both (a) and (b)
(d) None of the above

Or

In the given reaction,

$$NH_3 + RX \longrightarrow \underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} R_4N^{\oplus}X^-$$

Select an appropriate statement(s) about the reaction.
(a) In this reaction, NH_3 act as a nucleophile
(b) In this reaction, RX is the nucleophile
(c) $R_4N^{\oplus}X^-$ is called quaternary ammonium salt
(d) Both (a) and (c)

6. Calculate the molarity of solution of $CaCl_2$ if on chemical analysis it is found that 200 mL of $CaCl_2$ contains 3.01×10^{22} Cl^- ions
(a) 40 M
(b) 3.01 M
(c) 0.125 M
(d) 0.250 M

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7. Consider the data given below for a hypothetical reactions, $M \rightarrow N$

Time(s)	Rate of reaction (mol L^{-1} s^{-1})
0	4.20×10^{-4}
10	4.20×10^{-4}
20	4.20×10^{-4}
30	4.20×10^{-4}
40	4.18×10^{-4}

For the above data, the order of reaction is

(a) one (b) two
(c) three (d) zero

Or

In a first order reaction, reactant concentration 'C' varies with time 't' as

(a) C decreases with $\frac{1}{t}$

(b) $\log C$ decreases with $\frac{1}{t}$

(c) $\frac{1}{C}$ increases linearly with t

(d) $\log C$ decrease linearly with t

8. Standard reduction electrode potentials of three metals A, B and C are $+0.5$ V, -3.0 V and -1.2 V respectively. The reducing power of these metals are

(a) $B > C > A$
(b) $A > B > C$
(c) $C > B > A$
(d) $A > C > B$

9. For d^4 ions, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$, when

(a) $\Delta_o > P$ (b) $\Delta_o < P$
(c) $\Delta_o = P$ (d) $\Delta_o \geq P$

Or

Atomic number of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following inner orbital octahedral complex ions are diamagnetic?

I. $[Co(NH_3)_6]^{3+}$ II. $[Mn(CN)_6]^{3-}$
III. $[Fe(CN)_6]^{4-}$ IV. $[Fe(CN)_6]^{3-}$

Choose the correct option.

(a) II and III (b) I and IV
(c) I and III (d) II and IV

10. Which of the following functional groups is present in paper, cotton and sugar?

(a) $-NH_2$ group
(b) $-OH$ group
(c) RX group
(d) None of the above

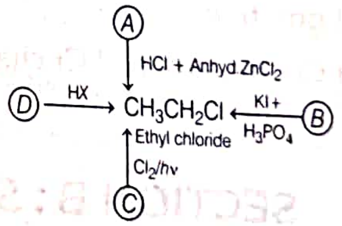
11. Identify A and B, C in the given sequence of reactions,

$$\underset{(B)}{H_2C{=}CH_2 + Br_2} \xrightarrow{A} \underset{(C)}{BrCH_2CH_2Br}$$

	(A)	(B)	(C)
(a)	CCl_4	Colourless	Reddish brown
(b)	CCl_4	Reddish brown	Colourless
(c)	CBr_4	Colourless	Reddish brown
(d)	CBr_4	Reddish brown	Colourless

Or

Consider the following flow chart ?



Here, A, B, C and D respectively are :

(a) $CH_3CH_2OH, CH_3CH_2OH, CH_3CH_3, CH_2{=}CH_2$

(b) $CH_3\underset{}{CH}(CH_3){-}OH, CH_3CH_3, CH_2{=}CH_2, CH_3CH_3$

(c) $CH_3-CH_3, CH_2=CH_2, CH_3-CH(CH_3)-OH, CH_3CH_2OH$

(d) $CH_3CH_2OH, CH_3CH_3, CH_3-CH(CH_3)-OH, CH_2=CH_2$

Answers

3. (b) **4.** (d) **5.** (c) or (d) **6.** (c) **7.** (d) or (d) **8.** (a) **9.** (b) or (c) **10.** (b) **11.** (b) or (a)

Assertion-Reason

In the following questions (Q.No. 12-16) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer ouf of the following choices.

(a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.
(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.
(c) Assertion is correct statement but Reason is incorrect statement.
(d) Assertion is incorrect statement but Reason is correct statement.

12. **Assertion** Conductivity always increases with decrease in concentration for strong and weak electrolytes.

Reason Number of ions per unit volume decreases on dilution.

13. **Assertion** Cr^{2+} is reducing, while Mn^{3+} is oxidising even though both have d^4 configuration.

Reason Configuration of Cr changes from d^3 to d^4.

Or **Assertion** Cr and Cu are extra stable elements in the $3d$-series.

Reason Half and completely filled set of orbitals are relatively more stable.

14. **Assertion** Boiling points of chlorides, bromides and iodides are considered to be higher than their corresponding hydrocarbons.

Reason Due to greater polarity and higher molecular mass, the intermolecular forces of attraction are weaker in halogen derivative as compared to hydrocarbon.

15. **Assertion** Aniline does not undergo alkylation and acetylation.

Reason Nitrogen of aniline acquires positive charge in the presence of $AlCl_3$.

16. **Assertion** p-nitrophenol is more acidic than phenol.

Reason Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

Answers

12. (d) **13.** (c) or (a) **14.** (c) **15.** (a) **16.** (a)

SECTION B : *Short Answer Type I Questions*

17. Give one chemical test to distinguish between the following.
(i) Ethyl alcohol and *sec*-propyl alcohol.
(ii) Ethanol and 2-propanol

18. How do you convert the following :
(i) Prop-1-ene to 1-fluoropropane
(ii) Chlorobenzene to 2-chlorotoluene

19. The rate of a first order reaction is 0.04 mol $L^{-1}s^{-1}$ at 10 min and 0.03 mol $L^{-1}s^{-1}$ at 20 min after initiation. Find the half-life of reaction. **[Ans. 24.06 min]**

Or The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact contained wood that had only 80% of the ^{14}C found in living tree. Estimate the age of the sample. **[Ans. 1845 years]**

20. Equal weights of two substances X and Y are dissolved in equal volumes of water. The osmotic pressure of the solution containing Y is five times the osmotic pressure of the solution containing X. What is the molecular weight of X if that of Y is 60? **[Ans.** $X = 300$ g mol^{-1}**]**

21. (i) How will you distinguish between glucose and sucrose?
(ii) Write relevant equation to convert fructose to osazone.

Or

(i) How will you convert glucose to osazone?
(ii) Which one of the following is a disaccharide?

22. Discuss the nature of bonding in the coordination entity, $[Co(C_2O_4)_3]^{3-}$ on the basis of valence bond theory. Also,

comment on the hybridisation and magnetic behaviour of the given entity.

23. How can the following conversion be brought about?

(i) 2-propanol to acetoxime.

(ii) Ethanol to acetone.

24. Deficiency of what vitamins cause following disease?

(i) Xerophthalmia

(ii) Beri-beri

Or

Mention the biological importance 'of insulin'

25. How would you achieve the following conversions?

(a) Nitrobenzene to aniline

(b) Benzyl chloride to 2-phenyl ethanamine

SECTION C : *Short Answer Type II Questions*

26. (i) Write the structure of 2-(2-bromophenyl) butane.

(ii) Haloalkanes react with KCN to form alkyl cyanides as the main product, while with AgCN isocyanides are formed as the main product. Explain.

Or

Identify the product formed when *n*-butyl bromide is treated with KCN in the presence of EtOH-H_2O. Write the mechanism involved in the above reaction.

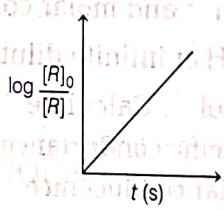
27. 0.05 M NaOH solution offered a resistance of 31.6 Ω in a conductivity cell at 298 K. If the cell constant of the cell is 0.367 cm^{-1}, calculate the molar conductivity of the NaOH solution.

28. Answer the following:

(i) Why is CO a stronger ligand than Cl ?

(ii) What is meant by crystal field splitting energy? How does the magnitude of splitting decide the actual configuration of *d*-orbitals in an octahedral field for a coordination entity?

29. For a chemical reaction $R \longrightarrow P$, the variation in the concentration of $\log \frac{[R]_0}{[R]}$ vs time '*t*' plot is given here.



For this reaction,

(i) What is the order of the reaction?

(ii) What is the unit of rate constant?

(iii) What is the slope of the curve?

Or The chemical reaction, $2O_3 \longrightarrow 3O_2$ proceeds as follows:

$$O_3 \rightleftharpoons O_2 + O \quad \text{(Fast)}$$

$$O + O_3 \longrightarrow 2O_2 \quad \text{(Slow)}$$

What should be the rate law expression?

30. Account for the following :

(i) What is the biological effect of denaturation on proteins?

(ii) What type of bonding helps in stabilising the α-helix structure of proteins?

SECTION D : *Long Answer Type Questions*

31. (a) Mention any two factors affecting the electrode potential of a metal.

(b) The specific conductance of a 0.01 M solution of acetic acid at 298 K is $1.65 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$.

The molar conductance at infinite dilution for H^+ ion and CH_3COO^- ion are $349.1\ \Omega^{-1}\ cm^2\ mol^{-1}$ and

$40.9\ \Omega^{-1}\ cm^2\ mol^{-1}$ respectively.

Calculate

(i) Molar conductance of the solution.

(ii) Degree of dissociation of CH_3COOH.

(iii) Dissociation constant for acetic acid.

Or

(a) Calculate : E_{cell} at 25°C for the reaction,

$$Zn + Cu^{2+}(0.20\ M) \longrightarrow Zn^{2+}(0.50\ M) + Cu$$

Given, $E^\circ_{(Zn^{2+}/Zn)} = -0.76\ V;$

$E^\circ_{(Cu^{2+}/Cu)} = 0.34\ V.$

(b) A 0.05 M NH_4OH solution offers the resistance of $50\ \Omega$ to a conductivity cell at 298 K. If the cell constant is $0.50\ cm^{-1}$ and molar conductance of NH_4OH at infinite dilution is $471.4\ \Omega^{-1}\ cm^2\ mol^{-1}$. Calculate

(i) Specific conductance

(ii) Molar conductance

(iii) Degree of dissociation

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32. (i) Explain the mechanism of nucleophilic attack on the carbonyl group of an aldehyde or a ketone.

(ii) An organic compound *A* (molecular formula = $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid *B* and an alcohol *C*. Oxidation of *C* with chromic acid also produced *B*. '*B*' on treatment with chlorine in the presence of small amount of red phosphorus and H_2O gave '*D*' and in presence of PCl_5, it gives '*E*'. On dehydration, *C* gave but-1-ene. Identify *A*, *B* and *C*, *D* and '*E*'.

Or

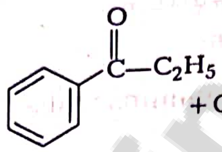
(i) How will you convert

(a) formaldehyde to methanol?

(b) benzaldehyde to *m*-nitrobenzaldehyde ?

(ii) Write the structures of *A*, *B* and *C* in the following :

(a) $CH_3CH{=}CHCHO + NH_2\overset{O}{\overset{\|}{C}}NHNH_2 \xrightarrow{H^+} A$

(b)  $+ CH_3NH_2 \xrightarrow{H^+} B$

(c) $CH_3COCH_3 \xrightarrow[KOH/glycol,\Delta]{H_2NNH_2} C$

33. (i) What happens, when

(a) iodide ion reacts with persulphate ion.

(b) iron (III) reacts with iodide ion.

(ii) Explain the following trends in the properties of the members of the transition elements.

(a) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.

(b) Silver atom has $3d^{10}$ -configuration, yet it is a transition element.

(c) The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple.

Or (i) An aqueous blue coloured solution of transition metal sulphate reacts with H_2S in acidic medium to give a black precipitate '*A*', which is insoluble in warm aqueous solution of KOH. The blue solution on treatment with KI in weakly acidic medium turns yellow and produces a white precipitate '*B*'. Identify the transition metal ion. Write the chemical reactions involved in the formation of '*A*' and '*B*'.

(ii) Describe the cause of the following variations :

(a) Although, Zr belongs to 4*d* and Hf belongs to 5*d*-transition series but it is quite difficult to separate them.

(b) Europium(II) is more stable than cerium(II).

(c) Cu(I) ion is not stable in an aqueous solution.

SAMPLE QUESTION PAPER 5

A HIGHLY SIMULATED SAMPLE QUESTION PAPER FOR CBSE CLASS XII

CHEMISTRY [Unsolved]

Instructions

1. There are 33 questions in this question paper. All questions are compulsory.
2. **Section A :** Q. No. 1 to 16 are Objective Type Questions. Q. No. 1 and 2 are Case Based Questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
3. **Section B :** Q. No. 17 to 25 are Short answer type I questions and carry 2 marks each.
4. **Section C :** Q. No. 26 to 30 are Short answer type II questions and carry 3 marks each.
5. **Section D :** Q. No. 31 to 33 are Long answer questions carrying 5 marks each.
6. There is no overall choice. However, an internal choices have been provided.
7. Use of calculators and log tables is not permitted.

SECTION A : *Objective Questions*

Case Based Questions

1. Read the passage given below and answer the following questions : (1×4=4)

Batteries consist of one or more electrochemical cells that store chemical energy for later conversion to electrical energy. Batteries are used in many day-to-day devices such as cellular phones, laptop computer, clocks, and cars. Batteries are compared of at least one electrochemical cell which is used for the storage and generation of electricity.

Though a variety of electrochemical cells exist, batteries generally consists of at least one voltaic cell. Voltaic cells are also sometimes referred to as galvanic cells. Chemical reactions and the generation of electrical energy is spontaneous within a voltaic cell, as opposed to the reactions electrolytic cells and fuel cells.

It was while conducting experiments on electricity in 1749 that Benjamin Franklin first coined the term "battery" to describe linked capacitors. However his battery was not the first battery, just the first ever referred to as such. Rather it is believed that the Baghdad batteries, discovered in 1936 and over 2,000 years old, were some of the first ever batteries, though their exact purpose is still debated.

Luigi Galvani (for whom the galvanic cell is named) first described "animal electricity" in 1780 when he created an electrical current through a frog. Though he was not aware of it at the time, this was a form of a battery. His contemporary Alessandro Volta (for whom the voltaic cell and voltaic pile are named) was convinced that the "animal electricity" was not coming from the frog, but something else entirely. In 1800, he produced the first real battery, the voltaic pile.

In 1836, John Frederic Daniell created the Daniell cell when researching ways to overcome some of the problems associated with Volta's voltaic pile. This discovery was followed by developments of the Grove cell by William Robert Grove in 1844, the first rechargable battery made of a lead-acid cell in 1859 by Gaston Plante; the gravity cell by Callaud in the 1860s; and the Leclanche cell by Georges Leclanche in 1866.

Until this point, all batteries were wet cells. Then in 1887 Carl Gassner created the first dry cell battery, made of a zinc-carbon cell. The nickel-cadmium battery was introduced in 1899 by Waldmar Jungner along with the nickel-iron battery. However, Jungner failed to patent the nickel-iron battery and in 1903, . Thomas Edison patented a slightly modified design for himself.

A major breakthrough came in 1955 when Lewis urry, an employee of what is now known as Energizer introduced the common alkaline battery. The 1970s led to the nickel-hydrogen battery and the 1980s to the nickel metal-hydride battery.

Lithium batteries were first created as early as 1912, however the most successful type, the lithium ion polymer battery used in most portable electronics today was not released until 1996.

(i) While charging the lead storage battery?

(a) $PbSO_4$ anode is reduced to Pb

(b) $PbSO_4$ cathode is reduced to Pb

(c) $PbSO_4$ cathode is oxidised to Pb

(d) $PbSO_4$ anode is oxidised to PbO_2

(ii) Which of the following statements is true for fuel cells?

(a) They are more efficient

(b) They are free from pollution

(c) They run till reactants are active

(d) All of the above

(iii) Which of the following reactions is used to make a fuel cell?

(a) $2H_2(g)+O_2(g) \longrightarrow 2H_2O(l)$

(b) $2Fe(s)+O_2(g)+4H^+(aq) \longrightarrow 2Fe^{2+}(aq) +2H_2O(l)$

(c) $2Pb(s)+PbO_2(s)+2H_2SO_4(aq) \longrightarrow 2PbSO_4(s)+H_2O(l)$

(d) $Cd(s)+2Ni(OH)_3(s) \longrightarrow CdO(s) +2Ni(OH)_2+2H_2O(l)$

Or

In a hydrogen-oxygen fuel cell, combustion of hydrogen occurs to

(a) generate heat

(b) create potential difference between the two electrodes

(c) produce high purity water

(d) remove adsorbed oxygen from electrode surfaces

(iv) On the basis of electrochemical theory of aqueous corrosion, the reaction occurring at the cathode is

(a) $O_2(g)+4H^+(aq)+4e^- \longrightarrow 2H_2O(l)$

(b) $H_2(g)+2OH^-(aq) \longrightarrow 2H_2O(l)+2e^-$

(c) $Fe(s) \longrightarrow Fe^{2+}(aq)+2e^-$

(d) $Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq)+e^-$

Answers

(i) (a) (ii) (d) (iii) (a) or (b) (iv) (a)

2. *Read the passage given below and answer the following questions :* (1×4=4)

One of the most important classes of biomolecules is carbohydrates. These include sugars, starch, glycogen, cellulose, etc. These are formed by plants under a process called photosynthesis and make up about 70% of plant material. Carbohydrates provide us food, clothing and shelter in the form of starch, cotton and wood respectively.
Earlier carbohydrates were called as hydrates of carbon $C_x(H_2O)_y$. But this definition is not applicable in all cases. Carbohydrates are also called saccharides. These can be monosaccharides, oligosaccharides and polysaccharides. Carbohyderates can also be classified as sugar and non-sugar. All the monosaccharides and oligosaccharides are sugar.

The polysaccharides are non-sugar. All those carbohydrates which reduce Tollen's reagent or Fehling solution are called reducing carbohydrates, while others which do not reduce these reagents are called non-reducing carbohydrates. All monosaccharides are reducing. All polysaccharides are non-reducing.

All carbohydrates can be hydrolysed except monosaccharides. Monosaccharides containing an aldehyde are called **aldoses** and those containing ketone are called **ketoses.**

In these questions (i-iv) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices :

(a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.

(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.

(c) Assertion is correct statement but Reason is wrong statement.

(d) Assertion is incorrect statement but Reason is correct statement.

(i) **Assertion** Sucrose is a non-reducing sugar.

Reason It has glycosidic linkage.

(ii) **Assertion** Glucose and fructose can be distinguished by Tollen's reagent.

Reason Glucose contains an aldehyde group while fructose contains a keto group.

(iii) **Assertion** Carbohydrates were earlier called as hydrates of carbon.

Reason Carbohydrates can be hydrolysed.

(iv) **Assertion** Starch is a non-sugar.

Reason Starch is polysaccharides.

Or

Assertion Cellulose is a carbohydrate.

Reason Cellulose has molecular formula, $(C_6H_{10}O_5)_n$.

Answers

(i) (b) (ii) (d) (iii) (b) (iv) (b) or (a)

Multiple Choice Questions

Following questions (No. 3-11) are multiple choice questions carrying 1 mark each :

3. According to postulates of Werner's theory for coordination compounds, which of the following is true?

(a) Primary valencies are ionisable.

(b) Secondary valencies are ionisable.

(c) Only primary valencies are non-ionisable

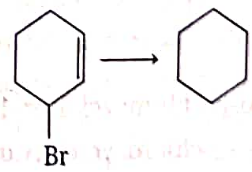
(d) Both primary and secondary valencies are non-ionisable.

4. Which of the following ions has the highest magnetic moment?

(a) Ti^{3+} (b) Sc^{3+}

(c) Mn^{2+} (d) Zn^{2+}

5. The transformation



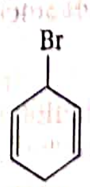
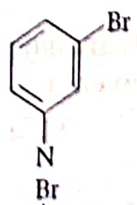
can be brought about using

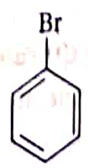
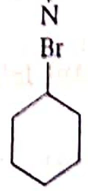
(a) Zn/H^+ (b) CuI

(c) Na (d) $(CH_3)_3CuLi$

Or

Which of the following compounds will produce a precipitate with $AgNO_3$?

(a)  (b) 

(c)  (b) 

6. Formic acid and acetic acid are distinguished by

(a) $NaHCO_3$

(b) $FeCl_3$

(c) Victor meyer test

(d) Tollen's reagent

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7. What is the coordination number in a square close packed structure in two dimensions ?

(a) 2 (b) 3

(c) 4 (d) 6

8. The incorrect IUPAC name is

(a) $CH_3—\underset{\underset{O}{\|}}{C}—\underset{\underset{CH_3}{|}}{CH}—CH_3$ (2-methyl-3-butanone)

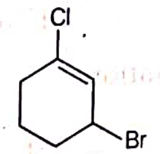
(b) $CH_3\underset{\underset{CH_3}{|}}{CH}—\underset{\underset{CH_2CH_3}{|}}{CH}—CH_3$ (2, 3-dimethyl pentane)

(c) $CH_3—C\equiv CCH(CH_3)_2$ (4 methyl-2-pentyne)

(d) $CH_3\underset{\underset{Cl}{|}}{CH}—\underset{\underset{Br}{|}}{CH}—CH_3$ (2-bromo-3-chlorobutane)

Or

The IUPAC name of the compound is



(a) 2-bromo-6-chlorocyclohex-1-ene

(b) 6-bromo-2-chlorocyclohexane

(c) 3-bromo-1-chlorocyclohexene

(d) 1-bromo-3-chlorocyclohexene

9. CH_3CH_2OH can be converted into CH_3CHO by

(a) catalytic hydrogenation

(b) treatment with $LiAlH_4$

(c) treatment with pyridinium chlorochromate

(d) treatment with $KMnO_4$

10. Which among the following is not amphoteric?

(a) Al^{3+} (b) Cr^{3+} (c) Fe^{3+} (d) Zn^{2+}

Or

Which of the following ion is diamagnetic?

(a) Nd^{3+} (b) La^{3+}

(c) Tb^{3+} (d) Er^{3+}

11. Which of the following will be most stable diazonium salt?

(a) $C_6H_5\overset{\oplus}{N_2}\overset{\ominus}{X}$ (b) $CH_3\overset{\oplus}{N_2}\overset{\ominus}{X}$

(c) $CH_3CH_2\overset{\oplus}{N_2}\overset{\ominus}{X}$ (d) $C_6H_5CH_2\overset{\oplus}{N_2}\overset{\ominus}{X}$

Or

The electrolytic reduction of nitrobenzene in strongly medium produces

(a) azobenzene

(b) aniline

(c) p-aminophenol

(d) azoxybenzene

Answers

3. (a) **4.** (c) **5.** (a) or (c) **6.** (b) **7.** (c) **8.** (a) or (c) **9.** (c) **10.** (b) or (c) **11.** (a) or (c)

Assertion-Reason

In the following questions (Q.No. 12-16) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer ouf of the following choices.

(a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.

(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.

(c) Assertion is correct statement but Reason is wrong statement.

(d) Assertion is incorrect statement but Reason is correct statement.

12. **Assertion** It is difficult to replace chlorine by —OH in chlorobenzene in comparison to that in chloroethane.

Reason Chlorine carbon (C—Cl) bond in chlorobenzene has a partial double bond character due to resonance.

13. **Assertion** Phenols give o- and p-nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.

Reason —OH group in phenol is o-,p-directing.

14. **Assertion** All naturally occurring α-amino acids except glycine are optically active.

Reason Most naturally occurring amino acids have L-configuration.

15. **Assertion** Chromium is a typical hard metal, while mercury is a liquid.

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Reason In Cr, there are six unpaired electrons, whereas in Hg, there is no unpaired electron.

16. **Assertion** α-hydrogen atoms of carbonyl compounds are acidic.

Reason The strong electron releasing effect of carbonyl group make the stabilisation of the conjugate base by the resonance.

Or

Assertion 2-butenal lacks enolisable H-atoms, α to carbonyl group still it has sufficient acidic character.

Reason The conjugate base of 2-butanal is stablised by resonance.

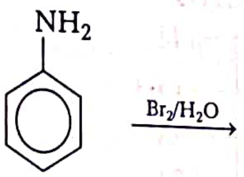
Answers

12. (a) **13.** (d) **14.** (b) **15.** (a) **16.** (c) or (a)

SECTION B : *Short Answer Type I Questions*

17. Complete the following reactions :

(i) $C_6H_5NH_2 + CH_3COCl \longrightarrow$

(ii) 

18. In a first order reaction, 10% of the reactant is consumed in 25 min. Calculate:

(*i*) The half-life period of the reaction.

(*ii*) The time required for completing 87.5% of the reaction.

[**Ans.** (i) $t_{1/2} = 173.25$ min ,(ii) $t = 519.90$ min]

19. The standard oxidation potential of Ni/Ni^{2+} electrode is 0.236 V. If this is combined with a hydrogen electrode in an acidic solution, at what pH of the solution will measured emf be zero at 25°C? (Assuming $[Ni^{2+}] = 1$ M) [**Ans.** ≈ 4]

20. Answer the following :

(i) Why Co^{2+} is easily oxidised to Co^{3+} in presence of a strong ligand.

(ii) Arrange the following complex ions in increasing order of crystal field splitting energy (Δ_o).

$[CrCl_6]^{3-}$, $[Cr(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$

Or (i) Write the IUPAC nomenclature of $[Cr(NH_3)_4Cl_2]^+$ and $[Co(en)_3]^{3+}$ complex.

(ii) Magnetic moment of $[MnCl_4]^{2-}$ is 5.92 BM. Give reason.

21. Give one chemical test to distinguish between the following pair of compounds:

(i) Acetone and phenol

(ii) Methanal and ethanal

22. Explain the following

(i) Why do transition metal ions possess a great tendency to form complexes?

(ii) The paramagnetic character in 3*d*-transition series elements increases upto Mn and then decreases.

Or

(i) Explain why transition metals form complex compounds?

(ii) Iron is ferromagnetic in nature. Explain why?

23. Account for the following :

Co(III) forms paramagnetic octahedral complex with weak field ligands whereas it forms diamagnetic octahedral complex with strong field ligands.

24. Account for the following :

(i) The enthalpy of atomisation is lowest for Zn in 3*d*-series of the transition element.

(ii) Transition metals form a large number of complexes.

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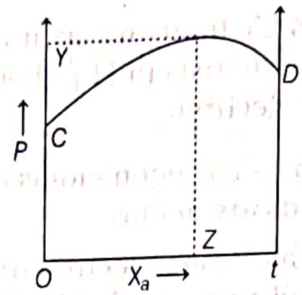
25. 0.5 M aqueous solution of sodium chloride show higher value of osmotic pressure than 0.5 M glucose solution at the same temperature. Why?

Or The pressure composition plot of a solution of two volatile liquids A and B is given below.

Answer the following by studying the plot carefully.



(i) Which liquid has higher boiling point?

(ii) What do points Y and Z represent?

SECTION C : *Short Answer Type II Questions*

26. (i) Complete the following reactions:

(a) $CH_3CH_2CH_2CH_2Cl \xrightarrow{\text{Alc.KOH}}$

(b) $CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 \xrightarrow{\text{Alc.KOH}}$

(ii) What is the type of the above reactions?

(iii) Predict the major product formed in reaction (b).

27. Give an example (equation) for each of the following name reactions

(i) Aldol condensation

(ii) Rosenmund's reduction

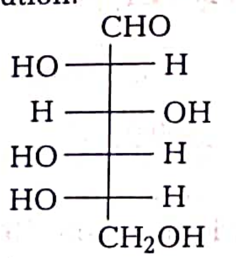
28. An aromatic compound A on treatment with aqueous ammonia on heating forms a compound B, which on heating with Br_2 and KOH forms a compound C of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

$$A \xrightarrow[\Delta]{Aq\,NH_3} B \xrightarrow[\Delta]{Br_2/KOH} \underset{(C)}{C_6H_7N}$$

Or (i) Illustrate the Gattermann reaction with an example.

(ii) Give chemical tests to distinguish between a primary and a secondary amine.

29. (i) The letters 'D' or 'L' before the name of a stereoisomer of a compound indicate the correlation of configuration of that particular stereoisomer. This refers to their relation with one of the isomers of glyceraldehyde. Predict whether the following compound has 'D' or 'L' configuration.



(ii) Aldopentoses named as ribose and 2-deoxyribose are found in nucleic acids. What is their relative configuration?

Or

(i) Monosaccharides contain carbonyl group hence are classified, as aldose or ketose.

The number of carbon atoms present in the monosaccharide molecule are also considered for classification. In which class of monosaccharide will you place fructose?

(ii) In nucleoside, a base is attached at '1' position of sugar moiety. Nucleotide is formed by linking of phosphoric acid unit to the sugar unit of nucleoside. At which position of sugar unit is the phosphoric acid linked in a nucleoside to give a nucleotide?

30. (i) Express the relation between conductivity of a solution cell constant.

(ii) Determine the values of equilibrium constant (K_C) and $\Delta G°$ for the following reactions as 25°C.

$$Ni(s) + 2Ag^+(aq) \longrightarrow Ni^{2+}(aq) + 2Ag(s),$$

$E° = 1.05$ V $\quad$ [$F = 96500$ C mol^{-1}]

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SECTION D : *Long Answer Type Questions*

31. (a) The molecular weights of sodium chloride and glucose are determined by the depression of freezing point method. Compared to their theoretical molecular weight, what will be their observed molecular weights when determined by the above method? Justify your answer.

(b) What will be the vapour pressure of a solution containing 5 moles of sucrose ($C_{12}H_{22}O_{11}$) in 1 kg of water, if the vapour pressure of pure water is 4.57 mm of Hg? (C = 12, H = 1, O = 16)

Or

(a) What is a colligative property? Give two examples.

(b) A solution of lactose containing 8.45 g of lactose in 100 g of water has a vapour pressure of 4.559 mm Hg at 0°C. If the vapour pressure of pure water is 4.579 mm Hg, calculate the molecular weight of lactose.

32. (i) For a reaction $A + B \longrightarrow P$, the rate is given by

$$\text{Rate} = k[A][B]^2$$

(a) How is the rate of reaction affected, if the concentration of B is quadrupled? **[Ans. 16 times]**

(b) What is the overall order of reaction if A is present in large excess ?

(ii) A first order reaction takes 23.1 min for 50% completion. Calculate the time required for 75% completion of the reaction. **[Ans. 46.2 min]**

Or

(i) In a reaction, if the concentration of the reactant R is quadrupled, the rate of reaction becomes sixty four times. What is the order of reaction? **[Ans. 3]**

(ii) A first order reaction has a rate constant of 0.0051 min^{-1}. If we begin with 0.10 M concentration of reactant, what concentration of reactant will remain in solution after 3 hours? **[Ans. 0.04 mol/L]**

33. An organic compound 'A' with molecular formula C_6H_6O reacts with zinc dust to give a hydrocarbon 'B', which upon reaction with CH_3Cl in the presence of anhydrous $AlCl_3$ gives 'C'. Compound C on oxidation with alkaline $KMnO_4$ gives compound D.

Compound A on further reaction with NH_3 in the presence of anhydrous $ZnCl_2$ gives 'E'. Identify the compound A, B, C, D and E, also justify your answer by giving relevant chemical equations.

Or

(i) How will you convert

(a) phenol into picric acid ?

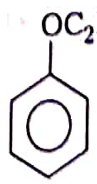
(b) cumene into phenol ?

(ii) Write the structures of A and B in the following reactions :

(a) 

$+ \ 2NaOH \xrightarrow[\text{(ii) HCl}]{\text{(i) 623 K, 320 atm}} A$

(b) $CH_3OCH_2Cl + CH_3MgI \xrightarrow{\text{Dry ether}} A + B$

(c) 

$+ \ HI \longrightarrow A + B$

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